SUPPLEMENTARY INFORMATION

Charge-Transfer Dynamics Controlled by Manipulating Dielectric Permittivities with Hyperbolic Metamaterial Structures as Solvent Analogues

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SI-I. Dyad Preparation ...............................................................................  1
SI-II. Grazing incidence wide angle X-ray scattering ...............................  1
SI-III. Further Optical Characterisations ....................................................  2
SI-III.1. Calculated Transmittance, Reflectance and Absorptance Spectra of HMM substrates .........................................................  2
SI-III.2. Steady State of the Dyad...........................................................  2
SI-III.3. Transient Data ...........................................................................  3
SI-III.3.a. CT Suggested Mechanisms ..................................................  3
SI-III.3.b. Sub-picosecond and Picosecond TA Spectra ............................  3
SI-III.3.c. Control Experiments: Ruling out Optical Excitation Field and Excitation Density Effects ..................................................  3
SI-III.3.e. Reflectance Mode: CT Dynamics of Dyad Films .................  4
SI-III.3.f. Reflectance Mode: Blend vs Dyad Transient Signal .........  5
SI-III.3.g. Control Experiments: CT Dynamics of Dyad Films on top of metal films over-coated with 10 nm Al2O3 ..................  6
SI-IV. General Model: Image Dipole Interactions Extended Marcus Theory .................................................................................................  6
SI-IV.1. Standard Parameters .................................................................  6
SI-IV.1.a. Reorganisation Energy .........................................................  6
SI-IV.1.b. Binding Energy ................................................................  7
SI-IV.2. Image Dipole Potentials ............................................................  7
SI-IV.2.a. Single Dipoles .................................................................  7
SI-IV.2.b. Distribution of Dipoles across D-A thin Films ...............  8
SI-IV.2.c. General Discussion around the Parameters used in the Theoretical Development .................................................................  9
SI-IV.3. Linking HMM perturbation and the dimensionless energy parameter .................................................................  9
SI-V. Further Analyses ........................................................................... 10
SI-V.1. CT Reaction rate ratios .............................................................. 10
SI-V.2. Impact of Dipole Orientations ................................................... 10
SI-V.2.a. Charge Separation .............................................................. 10
SI-V.2.b. Charge Recombination ......................................................... 10
SI-V.3. Assessing the C5 to C7 Reactation Rates Ratios ............... 10
SI-VI. Generalisation ............................................................................ 11
SI-VI.1. 2:1 Ratio P3HT:PC61BM Blends .............................................. 11
SI-VI.2. Comments on the Limits of the Solvent Analogy ................. 11
SI-VI.2.a. Metamaterial Structural Considerations ........................... 11
SI-VI.2.b. Image Dipole Non-Local Effects in the context of Common Optical HMM Properties ......................................................... 11
SI-VI.2.c. Solid State Image Dipole Non-Local Effects vs Solution Polarity Local Effects ................................................................. 12
SI-VI.3. Large Scaled Schematic Representation of the HMM Effect on Energy Diagrams ................................................................. 12
SI-VI.3.b. CT Parabola Shift .............................................................. 13
SI-VII. Glossary ................................................................................... 13
SI-VIII. References ............................................................................... 14

SI-I. Dyad Preparation

In a typical synthesis illustrated on the SI-Scheme below,¹ the dyad molecules were grafted as follows. A (300 mg, 0.36 mmol), B (217 mg, 0.36 mmol), zinc acetate (66.3 mg, 0.36 mmol) and imidazole (2.0 g) were added under stirring. The mixture was heated to 160 °C for 2 h under Ar and then cooled to room temperature. The solid mixture was dissolved in chloroform and was purified by column chromatography (silica gel, ethyl acetate/ hexane, 1:3-1:4), and recrystallized from chloroform to methanol to give Dyad (381 mg, 75 %) as a dark violet solid.

NMR δ (ppm) (500 MHz, CDCl3): 8.52-8.11 (8H, m, H arom), 7.54-7.37 (6H, m, H arom), 5.19 (1H, m, N-CH), 4.16-4.00 (14H, m, -O-CH2-, N-CH2), 2.27 (2H, m, H aliph), 1.94 (14H, m, H aliph), 1.73 (2H, m, H aliph), 1.64-1.24 (54H, m, H aliph), 1.01-0.96 (15H, m, H aliph), 0.96-0.84 (6H, m, H aliph), δc (ppm) (125 MHz, CDCl3) 163.126, 148.733, 134.178, 134.006, 130.679, 129.333, 128.814, 125.996, 125.943, 123.340, 123.270, 123.231, 123.161, 122.912, 122.627, 122.478, 107.001, 106.894, 106.698, 106.604, 106.573, 106.492, 96.705, 96.660, 96.511, 69.429, 69.347, 54.892, 40.642, 32.545, 32.004, 29.750, 29.404, 29.286, 29.005, 28.905, 28.811, 28.657, 28.553, 28.517, 27.795, 27.280, 26.866, 25.874, 22.770, 22.749, 14.293, 14.268, 14.222, HRMS calculated for C92H120N2O10Na+: 1435.884; found 1435.882. MALDI-TOF: calcd. for C92H120N2O10H+: 1413.902; found 1413.689. Elemental Analysis: calculated for C92H120N2O10: C, 78,15; H, 8.55; N, 1.98; O, 11.32. Found: C, 78.58; H, 8.74; N, 1.92; O, 11.06.

SI-II. Grazing incidence wide angle X-ray scattering

SI-Figure 1 presents a characteristic GIXS pattern of a dyad molecule thin film spincoated on aluminum oxide substrates and annealed at 120 °C for 2 hours. In the wide-angle region, the 1.4 Å⁻1 (4.5 Å) diffuse halo corresponds to the liquid-like structure of the aliphatic chains (h1), and the broad and intense in-plane reflection ~ 1.8 Å⁻1 (3.5 Å) along q_x, corresponds to the π-π stacking (h2) of the discotic mesogens. In the small-angle region, the sharp reflections in and out of the specular plane i.e. along q_z, are assigned to the reflections of the hexagonal columnar phase (Colh). The pattern proves a self-organization identical to the Colh pristine bulk structure, namely a phase of undifferentiated T/P columns. It also proves a spontaneous planar orientation of the columnar structure within the thin layer, consisting in domains of planar lying columns rows as demonstrated by the splitting of the first order reflection in spots at 0° and ±60° from the meridian and by the h_2 scattering located on the equator. The annealing step in the fluid state of the mesophase (120 °C) does logically not modify this already optimal orientation, but develops the long-range order similarly as in the bulk. The appearance of numerous dot-sharp higher order reflections then attest to the regularity of the structure and to the nearly perfect planar
orientation. This GIXS pattern is consistent with those obtained on silicon wafer, and showing also that in annealed films the dyad molecules self-organize in hexagonal columnar structures. The molecules are edge-on orientated on the substrate while the columns are oriented parallel to the surface. No specific changes of the GIXS patterns were observed in rotating the sample during the GIXS measurements, which suggests that there is no preferential alignment of columns.

**SI-Figure 1 |** GIXS pattern of a dyad thin film spincoated on Al2O3 surface from DCM solution, and annealed at 120°C for 2 h. Inset views: alignment of mixed triphenylene/perylene columns (red and black discs) on substrate (lying columns) and orientation of crystallographic axes (blue).

**SI-III. Further Optical Characterisations**

**SI-Figure 2 |** Calculated optical spectra of HMM substrates: a, transmittance. b, reflectance. c, absorptance for up to 4 metal-dielectric pairs.

**SI-III.1. Calculated Transmittance, Reflectance and Absorptance Spectra of HMM substrates**

The invariant imbedding method is a powerful tool for handling the electromagnetic wave propagation in one-dimensional inhomogeneous media. Maxwell’s equations were applied to the amplitude of the electric field. The exact differential equations satisfied by the reflection coefficient and the electric field amplitude were obtained with respect to medium size. These were supplemented with the initial conditions from Fresnel formulas. Using this method, we calculated the transmittance, reflectance and absorptance spectra of a range of HMM substrates. As the number of pairs is increased the transmittance decreases (SI-Figure 2 |b), which for the long and short wavelengths corresponds to an increase of the reflectance (SI-Figure 2 |b) and absorptance (SI-Figure 2 |c), respectively.

**SI-III.2. Steady State of the Dyad**

UV-vis absorbance and reflectance spectra were measured using a Hitachi U-3310 spectrophotometer and the absorbance was determined with the standard transmittance equation, \( A = - \log_{10} T \), and with fused silica substrates when needed. SI-Figure 3 |a presents the normalised absorption spectra of the TriPh, PerDi and dyad molecules as obtained in DCM solutions.

**SI-Figure 3 |** Dyad steady state absorbance measurements: a, in DCM solution of triphenylene (■), perylene diimide (◆) and dyad (■) molecules. b, of as-prepared and annealed dyad thin films on fused silica substrates. c, of annealed dyad thin films on HMM substrates.

Features of both TriPh and PerDi are easily identifiable in the dyad spectrum, even though the dyad is not the direct sum of the TriPh and PerDi. This is for instance visible in the peak ratios and widths. As discussed in the manuscript, once deposited the absorption spectra of the films still present characteristics of the TriPh and PerDi at high and low energy, respectively. These characteristics are broader than in solution as a result of π-π
interactions. Annealing alters the relative height of the PerDi peaks, which is consistent with the decrease of (0,1) vibronic peak relative to the (0,0) transition due to the cofacial stacking of PerDi in H-aggregates. Simultaneously, the relative growth of the absorbance above 600 nm corresponds to improved π-staking. Formation of an absorption band around 565 nm in aggregates of PerDi have been reported and associated with strong π-π interactions,5,6 which is consistent with the absorption tail herein observed and it suggests weaker π-π interactions within the core of the PerDi columns than in strongly aggregated PerDi films. This aggregation induces a very efficient quenching of the photoluminescence of both TriPh and PerDi moieties.

SI-Figure 3 presents the absorption spectra of annealed dyad films deposited on HMM substrates. These are the sum of the two components (dyad and HMM with different number of pairs), and within the experimental precision neither spectral shift nor broadening were observed, which is consistent with the literature.

SI-III.3. Transient Data

SI-III.3.a. CT Suggested Mechanisms

X-ray diffraction studies have shown that the triphenylene and the perylene bisimide units alternate in dyad film into different groups of stacked mesogens of same nature along a columnar axis long of about 30 units.1,7 This implies that only about 3% of the PerDi columns than in strongly aggregated PerDi films. Simultaneously, the relative growth of the peaks, which is consistent with the decrease of (0,1) vibronic interactions. Annealing alters the relative height of the PerDi and on the charge separation (τCS) and recombination (τCR) times obtained in transmittance mode TA.

SI-III.3.c. Control Experiments: Ruling out Optical Excitation Field and Excitation Density Effects

In the present system, effects such as exciton-exciton annihilation, exciton-charge annihilation, as well as bimolecular charge recombination could influence the measured CT dynamics. A decrease (increase) of the optical excitation field could indeed lead to a decrease (increase) of multi-particle interactions. To rigorously assess such potential effects, optical excitation field calculations as well as measurements under different excitation densities are necessary. We completed the former with the invariant embedded method,2-4 which we have already used to investigate the effect of optical field in organic solar cells.5 SI-Table 1 presents the optical calculated electric field and the fluence of the pump beam as a function of the substrate.

SI-Table 1. Influence of selected substrates and controlled incident 325 nm excitation power (P) on the square (i.e. intensity) of the integral of the optical field at the excitation wavelength normalised by the incident field |P|2, on the excitation fluence and on the charge separation (τCS) and recombination (τCR) times obtained in transmittance mode TA.

| Substrate | P (mW) | |F|2 | Fluence (µJ/cm2) | τCS (ps) | τCR (ps) |
|-----------|--------|--------|-----------------|-----------------|-------------|-------------|
| Al2O3 - dyad | 2.0 | 0.96 | 22.6 | 0.23 ± 0.05 | 226 ± 5 |
| 1p - dyad | 2.0 | 1.19 | 27.9 | 0.30 ± 0.05 | 256 ± 5 |
| 2p - dyad | 2.0 | 1.44 | 33.8 | 0.34 ± 0.05 | 277 ± 5 |
| 3p - dyad | 2.0 | 1.70 | 40.0 | 0.45 ± 0.05 | 327 ± 5 |
| 4p - dyad | 2.0 | 1.91 | 44.7 | 0.55 ± 0.05 | 391 ± 5 |
| Al2O3 - dyad | 0.5 | 0.96 | 5.7 | 0.22 ± 0.05 | 224 ± 5 |
| Al2O3 - dyad | 1.0 | 0.96 | 11.3 | 0.22 ± 0.05 | 222 ± 5 |
| Al2O3 - dyad | 2.0 | 0.96 | 22.6 | 0.23 ± 0.05 | 226 ± 5 |
| Al2O3 - dyad | 5.0 | 0.96 | 45.3 | 0.23 ± 0.05 | 227 ± 5 |

100 fs and 1 ps time interval. 2 with FS-dyad as a reference.

It can be clearly seen, that the excitation density increases with the number of pairs. To quantify the fluence dependence of the dyad transient absorption signal, TA measurements using different fluences were completed on fused silica substrates. The range of incident power was chosen to start from lower values and to reach the maximum fluence value obtained on the HMM structures. The normalised transient spectra presented SI-Figure 5 show that, within the fluence range used in the present study, the dynamics of the CS and CR processes in dyad film are independent of the excitation density.

In SI-Figure 5, a2 and b2, shifted transient data allow an easier visualisation of the curves and single exponential fittings show that the CT time constants are indeed independent of the fluence. The CS and CR characteristic times are presented in SI-Table 1. For comparison purposes, the data obtained on HMM structures at constant incident excitation power, and on fused silica exposed to different excitation incident power are plotted in SI-Figure 5 c1 and c2. These plots, showing constant CT dynamics on fused
SI-Figure 5 | Effect of Excitation Fluence on Transient Spectroscopy Measurements. Charge separation (a) and recombination (b) dynamics measured in transmittance mode as a function of time delays. Linear (a1,b1) and semi-log (a2,b2) scale for a range of excitation fluence on annealed dyad thin films deposited on fused silica substrates, note that to illustrate the signal variation, the scale of b2 ($\Delta T/T$) is inverted compared with the scale of a2 ($\Delta T/T + 1$). Symbols: experimental data points, full lines: single exponential fits. CS (c1) and CR (c2) characteristic times plotted as a function of the excitation fluence on fused silica (red disks, ) and HMM structures (CS: green square, ; purple diamonds, ).

silica and a progressive slowdown on HMM structures, illustrate further and without ambiguity that the fluence is not a key parameter to describe the CT kinetics herein reported and that the kinetic slowdown is directly correlated with a phenomenon induced by the HMM structure of the substrates. Consequently, these control experiments confirm that the transient CT measurements are not subject to trivial density dependent effects.

SI-III.3.d. Transmittance Mode: Summary of the HMM Impact on the CT Dynamics of Dyad Films

The data presented in Fig. 2b-c of the main text are replotted in SI-Figure 6 | a and b, in both linear (1) and semi-log (2) scales. SI-Table 2 summarises the values obtained by exponential analysis of CS and CR dynamics and plotted in Fig. 2b-c and Fig. 3 of the main text. All the transient spectra show a single exponential behaviour.

**SI-Table 2.** Charge separation ($\tau_{CS}$) and recombination ($\tau_{CR}$) times obtained by transmittance mode TA on selected substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\tau_{CS}$ (ps)</th>
<th>$\tau_{CR}$ (ps)</th>
<th>$\tau_{CS}/\tau_{CR}$ (x10$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$-dyad</td>
<td>0.23 ± 0.05</td>
<td>226 ± 5</td>
<td>1.02 ± 0.24</td>
</tr>
<tr>
<td>1 p - dyad</td>
<td>0.30 ± 0.05</td>
<td>256 ± 5</td>
<td>1.17 ± 0.19</td>
</tr>
<tr>
<td>2 p - dyad</td>
<td>0.34 ± 0.05</td>
<td>277 ± 5</td>
<td>1.24 ± 0.17</td>
</tr>
<tr>
<td>3 p - dyad</td>
<td>0.45 ± 0.05</td>
<td>327 ± 5</td>
<td>1.37 ± 0.13</td>
</tr>
<tr>
<td>4 p - dyad</td>
<td>0.55 ± 0.05</td>
<td>391 ± 5</td>
<td>1.41 ± 0.10</td>
</tr>
</tbody>
</table>

§ 100 fs and * 10 ps time interval.

SI-III.3.e. Reflectance Mode: CT Dynamics of Dyad Films

The consistency of the dynamics measured in transmittance and reflectance mode was verified for both CS and CR. The results are shown in the left and right columns, respectively, of SI-Figure 6 |. The TA signals vary as a single exponential and the quantitative analysis is summarised in SI-Table 3. Within the experimental precision, the transmittance and reflectance mode transient measurements present the same CS and CR characteristic times. The deviations from the transmittance mode are at a maximum of 10 and 5 % for CS and CR respectively. This demonstrates unambiguously that the dynamic alteration cannot be attributed to the measurement mode used to access the information but that this variation does result from the effect of the HMM structures located nearby the organic semiconductor dyad films.

**SI-Table 3.** Charge separation ($\tau_{CS}$) and recombination ($\tau_{CR}$) times obtained in reflectance mode TA measurements. $\Delta \tau_{CT}/\tau_{CT}$ relative variation of measurements in reflectance mode compared to those completed in transmittance mode.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\tau_{CS}$ (ps)</th>
<th>$\Delta \tau_{CS}/\tau_{CS}$ (%)</th>
<th>$\tau_{CR}$ (ps)</th>
<th>$\Delta \tau_{CR}/\tau_{CR}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$-dyad</td>
<td>0.21 ± 0.05</td>
<td>8.7</td>
<td>215 ± 5</td>
<td>4.9</td>
</tr>
<tr>
<td>1 p - dyad</td>
<td>0.27 ± 0.05</td>
<td>10</td>
<td>254 ± 5</td>
<td>0.8</td>
</tr>
<tr>
<td>2 p - dyad</td>
<td>0.34 ± 0.05</td>
<td>0</td>
<td>280 ± 5</td>
<td>-1.1</td>
</tr>
<tr>
<td>3 p - dyad</td>
<td>0.42 ± 0.05</td>
<td>6.7</td>
<td>324 ± 5</td>
<td>0.9</td>
</tr>
<tr>
<td>4 p - dyad</td>
<td>0.52 ± 0.05</td>
<td>5.5</td>
<td>393 ± 5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

§ 100 fs and * 10 ps time interval.
SI-Figure 6 | Transient Spectroscopy Measurements of annealed dyad thin films on HMM substrates. Charge separation (a, b) and recombination (c, d) dynamics measured in transmittance (a, c) and reflectance (b, d) modes as a function of time delays. Linear (1) and semi-log (2) scale for a range of HMM number of Ag/Al_2O_3 pairs, note that to illustrate the signal variation, the scale of c2 (ΔT/T) and d2 (ΔR/R) is inverted compared with the scale of a2 (ΔT/T+1) and b2 (ΔR/R+1). Symbols: experimental data points, full lines: single exponential fits.

SI-III.3.f. Transmittance Mode: Blend vs Dyad Transient Signal
SI-Figure 7 | presents the transient absorption signals measured for both the dyad and the blend of PerDi and TriPh deposited on fused silica and 4-bilayer HMM substrates. The characteristic times of charge separation and recombination and the fitted curves were obtained with the exponential based equations below:

\[ \Delta T/T(t) = \alpha \exp(-t/\tau_{CS}) - 1 \]  \hspace{1cm} (1)
\[ \Delta T/T(t) = -\alpha \exp(-t/\tau_{CR}) \] \hspace{1cm} (2)

Both CS and CR increase when the material is deposited on HMM substrates as compared with the signal observed on fused silica. As noticeable in SI-Table 4, the increase is however stronger in the case of the dyad than in the case of the PerDi and TriPh blend thin films.
electronic coupling, when compared to Al₂O₃, so that we can illustrate the recovery of the signal.

For both CS and CR, the plots in linear and semi-log scale, clearly show that regardless of the metal thickness the same CT dynamics is observed as demonstrated by the overlap of all the curves. The characteristic times deduced from single exponential fits are presented in SI-Table 5. These demonstrate that, within ~5%, i.e. of the order of magnitude of the uncertainty of the measurements and fits, there is no variation of the CT dynamics with different metal thicknesses. This is in good agreement with the model, which we developed and inserted in Marcus Theory, and which is presented in the following sections.

SI-IV. General Model: Image Dipole Interactions Extended Marcus Theory

SI-IV.1. Standard Parameters

Marcus theory describes non-adiabatic CT reaction rates, $k_{CT}$, in terms of activation Gibbs free energy, $ΔG_{CT}$, electronic coupling between the initial and final states (CT integral), $V_{DA}$, total reorganisation energy, $λ$, and thermal energy, $kT$.\(^\text{15-19}\)

$$k_{CT} = \left(\frac{4π^3}{h^2kT}\right)^{1/2} |V_{DA}| \exp\left[-\frac{ΔG_{CT}^*}{kT}\right]$$

$ΔG_{CT}^*$ relates to Gibbs free energy gain, $ΔG_{CT}$ and $λ$, leading to a parabolic variation of $k_{CT}$ with the driving force, $ΔG_{CT}$.

$$ΔG_{CT}^* = \frac{(λ + ΔG_{CT})^2}{4λ}$$

The semiclassical approach assumes that CT occurs at a transition states and neglects any tunnelling effect which could assist the transfer when vibrational modes of the initial and final states overlap.

We assumed the effect of the HMM on $ΔG_{CT}$ is a small perturbation, $Δλ_{HMM}$, when compared to Al₂O₃, so that we can write

$$ΔG_{HMM} = ΔG_{CT}^{Al₂O₃} + Δλ_{HMM}$$

SI-IV.1.a. Reorganisation Energy

The reorganisation energy includes two contributions: $λ_{intr}$ an intramolecular term accounting for vibrational, bond length and angles change within the reagents, and $λ_{env}$, accounting for reorientation and change of polarisation around the reagents upon CT. It can be expressed as

$$λ = λ_{intr} + λ_{env}$$

$$λ_{intr} = \frac{1}{2} \sum_j k_j \lambda_j$$

Assuming point charges, dielectric continuum description of the solvent and an isotropic system, $λ_{env}$ can be determined by the Born–Hush equation often used to describe solution CT.\(^\text{16,17}\)

$$λ_{env} = \frac{e^2}{4πε_0} \left[\frac{1}{2r_{D}^+} + \frac{1}{2r_{A}^-} - \frac{1}{R_{cc}}\right] \left(\frac{1}{ε_{optics}} - \frac{1}{ε_{static}}\right)$$

with $R_{cc}$, the center-to-center distance between the donor and the acceptor, $r_{D/A}^+$, the ionic radii of the donor and the acceptor respectively, $ε_{optics}$ and $ε_{static}$ the optical and static dielectric permittivities of the surrounding media, respectively. Whilst it falls beyond the scope of this work, it noticeable that the point dipole, homogeneous and isotropic media, center-to-center distance between the donor and the acceptor, spherical ions $r_{D/A}^+$, radii related hypotheses implied in equation (8) are not necessarily valid anymore in thin films for which the expression of $λ_{env}$ is not as simple as stated above.\(^\text{20-22}\) However, this is not essential in the context of a qualitative description of the phenomena herein reported. By analogy with solution related equations, we define

$$A_R = \frac{1}{R_{cc}} - \frac{1}{2r_{D}^+} - \frac{1}{2r_{A}^+} - \frac{1}{R_{cc}} - \frac{1}{R_{cc}} - \frac{1}{r_{cc}}$$

Let us note that taking for $R_{cc} ~ 1.91$ nm obtained from the GIXS measurements, and typical values of $r_c ~ 0.55$ nm,\(^\text{23,24}\) does lead systematically to $A_R < 0$. The effective ionic radii are model-dependent parameters, however it was shown that a reasonable fit to Born charging energies of aromatic ions is obtained when ionic radius is obtained from the molar volume of the neutral molecule,\(^\text{17}\) and that in the PerDi case the anion radii could be estimated geometrically from the distance from the center of the perylenebisimide to the nitrogen atom at its edge.\(^\text{25}\)
and by DFT calculations.\textsuperscript{25} It is, however, not necessary to detail the expression of $A_{1/8}$ in the context of the present analysis applied to films as we do not expect drastic changes of atomic positions for films on top of HMM and plain dielectric substrates. Consequently, $A_{1/8}$ should be reasonably independent of the substrates on which the D-A molecules are located and the expression above is a reasonable approximation. In the rest of this analysis, we will consider that the reorganization energy is not much altered.

**SI-IV.1.b. Binding Energy**

As for $\lambda_{exc}$, we note that $E_{cb}$ can relatively well expressed for solution based system by considering the difference in Coulomb energy when charges are at a set distance of one another and far apart, equation (10a). In the case of thin films, $E_{cb}$ is much harder to define in a simple manner, even though it can reasonably be associated with exciton binding energy in the case of charge separation (equation 10b).\textsuperscript{21}

$$E_{cb} = -\frac{e^2}{4\pi \varepsilon_0 \varepsilon_{eff} R_{cc}} \left( \frac{1}{R_{cc}^3} - \frac{1}{r_b} \right)$$  (10a)

$$E_{cb}^S = -\frac{1}{4\pi \varepsilon_0 \varepsilon_{eff}} \left( \sum q_\text{D}^a q_\text{A}^b - \sum q_\text{D}^a q_\text{D}^b - \sum q_\text{A}^a q_\text{A}^b \right)$$  (10b)

with $\varepsilon_{eff}$ dielectric permittivity of the environment (solvent or matrix) in which the CT is observed, $R_{cc}$ the center-to-center distance between the donor and the acceptor, $r_b$ the ionic radii and $2r_{ca} = |r_{D}^a + r_{A}^b - q_{DA}^a|$. The atomic charges and separation are, respectively, of the donor and acceptors in their relevant states with the sum running over all the atoms of the individual molecules.

We highlight the relevance of $\varepsilon_{eff}$ in both film and solution and for the sake of this analysis we give $E_{cb}$ the following general expression:

$$E_{cb} = -\frac{e^2 A_{1/8}}{4\pi \varepsilon_0 \varepsilon_{eff}}$$  (10c)

**SI-IV.2. Image Dipole Potentials**

**SI-IV.2.a. Single Dipoles**

To understand the dynamics of the CT experimental data, we analysed them within the Marcus theory framework including both a dipole formed in the dyad molecular structures and the image dipole potentials influenced by the HMM structures. These as illustrated in SI-Figure 9 |a and b, respectively.

$$U_0 = -\frac{q^2}{4\pi \varepsilon_0 d}$$  (11)

with $q$ the dipole charge, $d$ the distance between the hole and the electron ($d_{cld} = 2$ nm). Assuming this dipole interacts only with its image we added an interaction energy term to the total energy

$$U_{tot} = U_0 + U_{int} = \phi U_0$$  (12a)

with $U_{int}$ parallel $U_{int}^{\parallel} = -\frac{\beta^2}{4\pi \varepsilon_0 R^3}$ and $U_{int}^{\perp} = -\frac{2\beta^2}{4\pi \varepsilon_0 R^3}$ for a single metal interface, $R$ the distance between the dipole and the metal interface, and the dimensionless energy parameter $\phi$, such that $\phi > 1$ indicates a decrease of the total energy ($U_c$ and $U_{int}^{\perp} < 0$), hence a dipole stabilization due to the interaction with its image. By defining a non-local dielectric permittivity manipulated by image dipole interactions, including the dipole-HHM interface distance dependence, we then recover the simple form of the total energy of the dipole, equations (11) and (12b), and we identify $\phi$ with the inverse of the image dipole interactions manipulated non-local dielectric permittivity of the medium in which the dipole is located, equation (13a).

$$U_{tot} = \frac{-\beta^2}{4\pi \varepsilon_0 \varepsilon_{eff} d}$$  (12b)

$$\phi = \frac{1}{\varepsilon_{eff}}$$  (13a)

This image dipole interactions manipulated non-local dielectric permittivity, $\varepsilon_{eff}$, is a direct function of the structure of the substrate on top of which the dipole is positioned. In a 1 pair HMM, $\phi$ depends on the dipole orientation, $\gamma$, with respect to metal interface as illustrated in SI-Figure 9 |c. It can be written as

$$\phi_{\gamma}^{\parallel} = 1 + \frac{1}{8(r + h)^3}$$  (13b)
$$\phi_{\gamma}^{\perp} = 1 + \frac{1}{4(r + h)^3}$$  (13c)

where $r = z/d$ and $h = a/d$, with $a$ and $z$ the dielectric layer thickness (half period of the HMM) and the dipole-dielectric interface separation, respectively, as defined in SI-Figure 9 |c. In case of multilayered structures as herein investigated the variation of the dimensionless energy parameter, $\phi$, from a N-1 pair structure to a N pair HMM can be written as

$$\phi_{\gamma}^{Np} = \phi_{\gamma}^{(N-1)p} = \frac{1}{[2r + 2(N-1)] \psi + \psi_{\gamma}^{Np}}$$  (14)

where the second term corresponds to interactions between image dipoles and $\psi$ is a series which depends on the dipole orientation

$$\psi_{\gamma}^{Np} = \sum_{i=2}^{N} \frac{1}{(i-1)^3} \approx -1.2$$  (15a)
$$\psi_{\gamma}^{Np} = \sum_{i=2}^{N} \frac{2}{(i-1)^3} \approx 2.4$$  (15b)

Both series converge for $N >> 1$ towards -1.2 and 2.4, respectively, which suggests that the interaction energy will also converge with the number of pairs. The resulting variation of the dimensionless energy parameter as a function of the normalized distance from the HMM is shown in SI-Figure 10 |a for a parallel and perpendicular orientation of the dipole.

SI-Figure 10 |a illustrates that regardless of the dipole orientation and the number of pairs, $\phi$ displays a monotonic variation as a function of the distance from the AlO$_3$ interface. The difference between two consecutive pairs converges quickly with the
The false-color plots of the dimensionless energy parameter show a continuous variation of the orientation of the dipoles and the relative distance from the interface with the HMM substrate for both 2 pair and 4 pair HMM, SI-Figure 11 a and b respectively. SI-Figure 11 c presents cross-sections of 4 pair HMM φ variation. One can notice that, for constant b values, there should be no strong impact from reducing the metal volume fraction, at least until the image dipole description stops being valid, or experimentally when the layer thickness is below the metal percolation threshold.

**SI-IV.2.b. Distribution of Dipoles across D-A thin Films**

We took into account the GIXS data which indicates that the donor and acceptor when organised in columns are not in direct contact with the dielectric and instead are isolated from it by the alkyl chain melt of thickness ℓ = 0.85 nm. Assuming a homogeneous distribution of the columns, we integrated φ over the thickness of the dyad layer, L = 40 nm, to obtain Φ:

\[
Φ = \frac{1}{L-ℓ} \int_ℓ^{L-ℓ} φ_i dz
\]

As illustrated in SI-Figure 12 |, Φ is a function of the average orientation of the dipoles. ΔΦ is simply the difference between the values obtained for any substrate and for Al₂O₃, while φᵢ is given by the equations (13).

**SI-Figure 11 | Dimensionless energy parameter**

False-color plot of the variation of the dimensionless energy parameter as a function of the normalized dipole-HMM interface distance and the orientation of the dipole for 2 pair (a) and 4 pair (b) HMM, the dashed line corresponds to selected values presented in (c).

number of pairs as set by the series described in eq. 5a and b and as illustrated in SI-Figure 10. Positive values indicate that a dipole is stabilized by its image. In this context, parallel and perpendicular orientations display very different behaviors. For a large number of pairs, a dipole with a parallel orientation is stabilized near the interface but destabilized further away: the higher the number of pair and the closer to the interface the destabilization occurs. In contrast, a parallel dipole for a single pair and a perpendicular dipole for any number of pairs are always stabilized regardless of their distance from the HMM.

This suggests that the dipole distribution might not be isotropic within the film, as those which are perpendicular to the substrate would be stabilized by their images, whereas those parallel to the HMM would face an unfavorable energy landscape. Keeping the orientation as a tunable parameter, the dimensionless energy parameter is written as a function of perpendicular and parallel contributions. This is graphically presented in SI-Figure 11 | for a range of dipole orientations.

**SI-Figure 10 | Dimensionless energy parameter**

(a) variation for 1 to 4 pair HMM and b, difference between two consecutive number of pairs as a function of the normalized distance from the Al₂O₃ interface. Parallel (1) and perpendicular (2) orientation of the dipole with respect to the HMM substrate.

Δ ≤ 1 when the dipole distribution is isotropic but keeps increasing with the number of pairs when

\[
Δ = \frac{1}{ε_{Al₂O₃}} - \frac{1}{ε_{HMM} - ε_{Al₂O₃}}
\]

with εᵩ the non-local dielectric permittivity manipulated by HMM image dipole interactions integrated over the thickness of the dyad thin film, εᵩᵢ is a specific location within the dyad film, ℓ the thickness of the dyad film, ℓ the thickness of the alkyl melt separating the donor and acceptor columns from the Al₂O₃ top interface of the substrates, z the distance from the top interface of the substrate to the dipole.

SI-Figure 13 | a illustrates the impact of the dipole orientation on ΔΦ. Its values plateau for p ≥ 2 when the dipole distribution is isotropic but keeps increasing with the number of pairs when
dipoles are more perpendicular to the substrate ($\gamma = 0$). We note that implicitly the assumptions include that i) the dyad hexagonal columnar structure is not essential to the observed phenomenon, ii) as most often the case, magnetic interactions are much smaller than electrostatic ones, iii) there is no specific effect linked to plasmon resonance, iv) dipoles are made of point charges separated by a constant distance, v) there is a low and somehow uniform dipole density interacting with their images only, and vi) the dipole orientation and density are independent of the number of bilayer pairs. The first assumption is validated by the fact that the CT characteristic times are increased even in the case of a simple donor-acceptor blend in which column structure will not be driven by the molecular grafting of the two moieties otherwise forming a dyad molecule. The second assumption is most often fulfilled. The third could be influenced by the polarization of the beams, which in the context of our transient absorption cannot be altered much due to the weak signal already measured in the current configuration. The remaining three assumptions are harder to discuss in the present experimental context and the laser fluences used in this study, which were selected to optimize the detected signal.

SI-IV.2c. General Discussion around the Parameters used in the Theoretical Development

The theoretical considerations herein developed do not aim at providing any quantitative prediction, but as for most theoretical approaches, they aim at establishing a qualitative agreement with experimental data, while also bringing qualitative predictive insights. One difficulty of such theoretical developments is to lift any suspicion of fudging the model with free parameters to eventually fit the experimental data. Beyond the familiar components of Marcus theory presented in SI-equations (3) to (10), the basis of the present theoretical development is that, as illustrated in SI-Figure 12, a dipole oriented parallel to the surface is stabilised by its image but the dipole orientation and density are independent of the number of bilayer pairs. The first assumption is validated by the fact that the CT characteristic times are increased even in the case of a simple donor-acceptor blend in which column structure will not be driven by the molecular grafting of the two moieties otherwise forming a dyad molecule. The second assumption is most often fulfilled. The third could be influenced by the polarization of the beams, which in the context of our transient absorption cannot be altered much due to the weak signal already measured in the current configuration. The remaining three assumptions are harder to discuss in the present experimental context and the laser fluences used in this study, which were selected to optimize the detected signal.

SI-IV.3. Linking HMM perturbation and the dimensionless energy parameter

In first approximation, we considered the Gibbs free energy of photo-induced electron transfer for a CT state formation

$$\Delta G_{\text{CS}} = (h v_{\text{ox-D}} - E_{\text{ox-D}}) - h v_{\text{red-A}} + E_{\text{Ch}}$$

(18a)

where $v_{\text{ox-D}}$ and $v_{\text{red-A}}$ are the oxidation and reduction potentials, respectively, $e$ is the elementary charge, $E_{\text{ox-D}}$ is the excited state energy of the donor and $E_{\text{Ch}}$ is the electrostatic work accounting for Coulombic attractions in both the reactants and products and the solvation energy in a matrix. $CS$ and $CR$ are linked through the following equation.

$$\Delta G_{\text{CR}} = -\Delta G_{\text{CS}} - E_{\text{ox-D}}$$

(18b)

Plasmonic and HMM structures are known to alter both the photonic density of states, hence the radiative dynamics,28,33 and electric and magnetic dipoles, hence angular dependent emission,34,35 of chromophores located near or inside these structures. However and to the best of our knowledge, the excited state energy it-self has not been shown to be affected by such substrates. We then considered that the oxidation and reduction potentials were not influenced by the multi-layered substrates. As a consequence, comparing equations (5) and (18) we identified the perturbation as

$$\delta \Delta G_{\text{CS}} = \delta \Delta E_{\text{CS}} = -\delta \Delta G_{\text{CR}}$$

(19a)

with the Coulomb interactions varying between dielectric and HMM substrates. Using equations (10c) and emphasizing the role of the dipole orientation lead to the following expression

$$\delta \Delta G_{\text{CS}} = -\delta \Delta E_{\text{CS}} = -\Delta \Phi_{\text{HMM}} \frac{\varepsilon^2}{4\pi\varepsilon_0} \Delta \gamma$$

(19b)

with $\Delta \gamma$ having the dimension of the inverse of a distance and not expected to be drastically altered by the substrates. More importantly we stress that according to the simple considerations described above, any charge transfer alterations due to presence of an HMM substrates should be a function of the variation of the non-local dielectric permittivity, manipulated by image dipole interactions, when comparing plain and nanostructured substrates.

SI-V. Further Analyses

SI-V.1. CT Reaction rate ratios

Using equations (3), (4) and (5), the logarithm of the HMM to $\text{Al}_2\text{O}_3$ CT reaction rate ratio can be expressed as the sum of a
constant, as well as a linear and a quadratic term in $\Delta G_{\text{HMM}}$, which is defined in equation (19).

$$\ln \frac{k_{\text{HMM}}}{k_{\text{CS}}} = -\sigma_{\text{CT}} [2(\lambda_{\text{CT}} + \Delta G_{\text{CT}}^{\text{AlO}_3}) \Delta \xi_{\text{CT}} + \Delta \xi_{\text{HMM}}^2] + \text{const.}$$  

(20)

with $\sigma_{\text{CT}} = (4\zeta_{\text{HMM}} kT)^{-1}$. Equation (20) applies to both CS and CR. We assumed that the reorganisation energy is relatively unaffected by the presence of the HMM. This is supported by the consistency between the experimental data and the analysis. To quantify the reorganisation energy would require, for instance, a quantum-chemical treatment, which goes beyond the scope of the present work.

SI-V.2. Impact of Dipole Orientations

SI-V.2.a. Charge Separation

By neglecting the 2nd order perturbation, then the logarithm of the experimental CS ratios as a function of $\Delta \Phi$ can be written as:

$$\ln \frac{k_{\text{HMM}}}{k_{\text{CS}}} = -\frac{1}{\Delta \xi_{\text{CS}}} [2(\lambda_{\text{CS}} + \Delta G_{\text{CS}}^{\text{AlO}_3}) \Delta \xi_{\text{CS}} + \Delta \xi_{\text{HMM}}^2] + \text{const.}$$  

(21)

with $\zeta_{\text{CS}} = -\frac{e^2}{4\pi \epsilon_0} [(\lambda_{\text{CS}} + \Delta G_{\text{CS}}^{\text{AlO}_3})/2 \lambda_{\text{CS}} kT]^{1/2}$.

Whilst a small contribution of $\Delta \Phi^2$ cannot be excluded, it does appear to be smaller than $\Delta \Phi$ at least for the experimental data accessible with this system. Interestingly, the slope on Figure 4c is positive, meaning that $\zeta_{\text{CS}}$ should be negative. As the term $\lambda_{\text{CS}} + \Delta G_{\text{CS}}$ is positive in the normal region, $\lambda_{\text{CS}}$ should be negative.

SI-V.2.b. Charge Recombination

We can show that CS is in the normal region, whereas CR is in the inverted region and close to the barrierless point. Hence $\lambda_{\text{CR}} + \Delta G_{\text{CR}} = 0$, so that equation (20) applied to CR should be:

$$\ln \frac{k_{\text{HMM}}}{k_{\text{CR}}} = -\frac{1}{\Delta \xi_{\text{CR}}} [2(\lambda_{\text{CR}} + \Delta G_{\text{CR}}^{\text{AlO}_3}) \Delta \xi_{\text{CR}} + \Delta \xi_{\text{HMM}}^2] + \text{const.}$$  

(22)

with $\zeta_{\text{CR}} = \frac{1}{4\pi \epsilon_0} [2^{1/2} \lambda_{\text{CR}} kT] ^{-2}$.

The quadratic dependence with $\Delta \Phi$ is verified and the curves present a positive slope as expected from the sign of $\zeta_{\text{CR}}$.

For the sake of the argument, the CR data variation was also tested for $\Delta \Phi$ as illustrated in equation (23).

$$\ln \frac{k_{\text{HMM}}}{k_{\text{CR}}} = -\frac{1}{\zeta_{\text{CR}}} [2(\lambda_{\text{CR}} + \Delta G_{\text{CR}}^{\text{AlO}_3}) \lambda_{\text{CR}} kT]^{-2} + \text{const.}$$  

(23)

with $\zeta_{\text{CR}} = \frac{e^2}{4\pi \epsilon_0} [(\lambda_{\text{CR}} + \Delta G_{\text{CR}}^{\text{AlO}_3})/2 \lambda_{\text{CR}} kT]^{1/2}$.

SI-Figure 14 | presents the variation of the CR characteristic times as a function of the dimensionless energy parameter integrated over the thickness of the dyad film. The line is guide for the eyes showing that there no linear dependence.

SI-Figure 14 | Evaluation of the validity of a linear variation of the CR characteristic times on a semi-log plot as a function of the dimensionless energy parameter integrated over the thickness of the dyad film. The line is guide for the eyes showing that there no linear dependence.

SI-V.3. Assessing the CS to CR Reaction Rate Ratios

Assuming both that the electronic coupling is independent of the CT phenomena under consideration (i.e. identical for CS and CR) for all the substrates, and that the reorganisation energy is independent of the substrate, while nonetheless being sufficiently different between CS and CR, then combining equations (1), (2) and (3) leads to the equation (24). In that expression, the logarithm of the CS to CR reaction rate ratio still contains a linear term and a quadratic term of the perturbation $\Delta \xi_{\text{CT}}^\text{HMM}$, as shown below.

$$\ln \frac{k_{\text{CR}}}{k_{\text{CS}}} = a_0 + a_1 \Delta \Phi_{\gamma}^\text{HMM} + a_2 \Delta \Phi_{\gamma}^\text{HMM}^2$$  

(24)

with

$$a_0 = \frac{1}{2} \ln \left( \frac{\lambda_{\text{CS}}}{\lambda_{\text{CR}}} \right) + \frac{1}{4kT} [2(\lambda_{\text{CS}} - \lambda_{\text{CR}}) + 4\Delta G_{\text{CS}}^{\text{AlO}_3} + 2E_{\text{ex-D}}] + \frac{\lambda_{\text{CS}}^{2} \lambda_{\text{CR}}^{2}}{4\pi \epsilon_0}\frac{\lambda_{\text{CS}}^{2} - \lambda_{\text{CR}}^{2}}{2}\frac{1}{kT}$$

and

$$a_1 = \left[ 2 + \frac{1}{\lambda_{\text{CS}}} \frac{1}{\lambda_{\text{CR}}} \frac{1}{4\pi \epsilon_0} \frac{E_{\text{ex-D}}}{3\lambda_{\text{CR}}} \frac{1}{kT} \lambda_{\text{CR}}^{2} \right] \lambda_{\text{CR}}$$

and

$$a_2 = \left[ \frac{1}{\lambda_{\text{CS}}} \frac{1}{\lambda_{\text{CR}}} \frac{1}{4\pi \epsilon_0} \frac{1}{kT} \lambda_{\text{CR}}^{2} \right] \lambda_{\text{CR}}^{2} \frac{1}{4kT}$$

The quadratic term driven by the coefficient $a_2$ should only cancel when the CS and CR reorganisation energies are identical, which is unlikely. The linear term driven the coefficient $a_1$ is not expected to cancel, except in very exceptional situations.

SI-Figure 15 |a and b display the variation of the logarithm of the CS to CR reaction characteristic time ratio as a function of $\Delta \Phi$ and $\Delta \Phi^2$, respectively. However, as CS and CR have both increased characteristic time, their ratio drops the overall variation, which consequently gives way for the relative
uncertainties of the two characteristic times to overshadow any \( \Delta \Phi \) linear or quadratic variation. We clearly see that the ratio is not equal to a constant but this do not allow us drawing any reliable conclusion. Other systems should be investigated in the future to assess to which extent equation (24) is valid.

**SI-VL. Generalisation**

**SI-VL.1. Ratio P3HT:PCBM Blends**

The generality of the effect of the HMM substrates on the CT kinetics is not only evident from the modelling based on the image dipole extended Marcus theory we presented above, but it was also verified through the use of the P3HT:PC60BM, which a standard polymer blend extensively studied in the context of bulk hetero-junction solar cells.

The P3HT:PC60BM samples were probed at 680 nm to allow larger static value and, at this wavelength, it is the cationic P3HT which is mostly probed.37,38 CS occurred too fast to be reliably measured with our set-up. However, the charge recombination could be measured and its TA signals measured in transmittance mode are presented in SI-Figure 16 A. The kinetic of CR was fitted with two characteristic times. We note however that 800 ps is the longest time delay accessible to our setup and that the shortest CR values which were fitted are not reliable due to the 100 fs time interval, so that only the longest CR times were extracted, plotted in SI-Figure 16 B as well as summarised in SI-Table 6.

**SI-VL.2. Comments on the Limits of the Solvent Analogy**

**SI-VL.2.a. Metamaterial Structural Considerations**

It is important to note that the effect herein observed is applicable to a wider range of metamaterials than just hyperbolic metamaterial structures. In section SI-VL.1, we demonstrated that it applies to a wider range of donor and acceptor compounds than bridged dyad molecules as illustrated with P3HT:PCBM blends.

In addition, we note that the formalism of effective dielectric permittivity can adequately describe the dielectric response inside the volume of metamaterials.40 However, in the present work, we stress that when metamaterial structures are located nearby donor-acceptor compounds, they affect charge transfer reactions in an apparently similar manner as modifying the dielectric permittivity of a solvent would.

**SI-VL.2.b. Image Dipole Non-Local Effects in the context of Common Optical HMM Properties**

The onset of the transition from transverse positive to transverse negative occurs at 3.39 eV (366 nm), which can be calculated with the equations below and is presented in SI-Figure 17 |

\[
\frac{E_x}{E_m} = \frac{f_x E_m}{f_d E_d} + \frac{(1-f_x)E_d}{(1-f_d)E_m} \quad \text{(25a)}
\]

\[
E_m = \frac{E_x}{f_x E_m + (1-f_x)E_d} \quad \text{(25b)}
\]

\[
\rho = \frac{t_m}{t_m + t_d} = \frac{t_m}{t_m + \alpha} \quad \text{(25c)}
\]

with \( E_x \), \( E_m \), \( E_{x-d} \) the permittivity of the metal, dielectric, and HMM structure. \( f_x \) is the filling factor, while \( t_m \) and \( t_d \) are the thicknesses of the metal and dielectric films, respectively. Noticeably, these considerations are relevant to what we term as HMM properties; however, we stress that our manuscript systematically and purposely refers to “HMM substrates” and “HMM structures”, not to “HMM properties”. Indeed, the non-local effect we report relies on dipole image interactions and is then independent of the optical phase diagram and the polarization, which both are relevant to an effective medium description and its hyperbolic energy-momentum dispersion relation.31,42
As a result, we stress that in the present quasi-static model we developed, the energy onset calculated above should have no impact on the CT dynamic modulation, neither should the polarisation which is also known to affect HMM properties. In contrast, the image dipole interactions do affect CS and CR processes with a high sensitivity to the configuration of multilayer stacks such as the number of metal-dielectric pairs. Consequently, changing the fill factor, hence the energy transition onset, is expected to have little impact on the CT dynamic alterations associated with the HMM substrate structure. Limiting cases can however be anticipated, when the metal or the dielectric films become too thin. In the latter case, an extremely thin dielectric layer could allow electrical charges to flow from one metal layer to another, which consequently would not support any more isolated image dipoles. We note that this thickness threshold will likely vary with the dielectric material, as well as the fabrication pathway, which could affect the uniformity of the dielectric layer, hence the thickness at which a short-circuit will occur. In the case of the metal, the films ought to be continuous otherwise the image dipoles as we have described them would not hold, which evidently sets the metal percolation as a limit to be careful about.

SI-VL.2.c. Solid State Image Dipole Non-Local Effects vs Solution Polarity Local Effects

In the case of the solvents, the dependence of charge transfer rates on their dielectric properties is well established.\(^{43-46}\) The main mechanism relies on the stability of the dipole moment of ground and/or excited energy levels of dyes molecules affected by a solvent polarity, i.e. its dielectric constants or equivalently its permittivity. Using different solvents implies that the dyes are immersed in environments of different dielectric permittivity, which induce different stabilizations of the excited state, and result in the well-known variation of the charge transfer rate. The immersion the dyes in a solvent corresponds to a local effect of the dielectric permittivity.

However, in case of thin film sitting on top of HMM substrates, the mechanism altering charge transfer processes is completely different. It relies on image dipole interactions to tune the stability of charge transfer states. This is a non-local effect of the nearby metamaterials, which has not been reported so far. Then, assuming an electrostatics approximation, the image dipole interactions are inserted in the dielectric permittivity as part of the formalism aiming at facilitating the mathematical description of the phenomenon. In that sense, using "effective" to qualify the resulting dielectric permittivity is convenient but might eventually lead to some confusion. For this reason, we labelled \(\hat{\epsilon}_{dl}\) as the non-local dielectric permittivity manipulated by image dipole interactions.

We also note that using HMM structures in this context also comes with the interests of not affecting the compounds organisation and morphology, not facing solubility and aggregation concerns, potentially reducing the reliance chemical engineering work and paves the way towards numerous solid state investigations and applications. This is where the analogy with a solvent stops: the effect and the formalism are comparable but the underlying science is very different.

SI-VL.3. Large Scale Schematic Representation of the HMM Effect on Energy Diagrams

SI-VL.3.a. Dynamic-Driving Force Marcus Diagram

As described briefly in the main text, SI-Figure 18 | illustrates the variation of the CT rates as a function of the ratio of the driving force (-\(\Delta G\)) and reorganisation energy. The image dipole interactions associated with the presence of the HMM is seen to be associated with a decrease and an increase of \(-\Delta G/\lambda\) for CS and CR respectively.

The SI-Figure 18 reproduces on a larger scale the Figure 5c2. It presents energy level as a function of the reaction coordinates. \(S_0\) and \(S_1\) are the standard ground and first excited states of the donor, and CT is the charge transfer state as presented on Marcus diagram. More original is CT\(^{HMM}\), which is the charge transfer state shifted under the influence of the image dipole interactions resulting from the nearby HMM. Let us see why in the case of the dyad molecule, CT\(^{HMM}\) is shifted towards higher energy. The difference between the lowest energies of the initial and final states corresponds to the energy gain, i.e. driving force, mentioned in equation (4). These are represented by the coloured arrows, purple and blue for the simple dielectric \((p = 0)\) and HMM substrates \((p > 0)\), respectively.

SI-VL.3.b. Schematic representation of the effect of HMM substrates on the dependence of the logarithm of the CT rates \((k_{CT})\) with the driving force \((-\Delta G)\) normalised with the reorganisation energy \((\lambda)\). The red dashed line represents the barrierless point. The pink and blue dots are the CT rates on standard and HMM substrates, respectively, the direction of the arrow indicates the impact on \(-\Delta G/\lambda\) and \(k_{CT}\) of the HMM substrate structure.
SI-VI.3.b. CT Parabola Shift

The semiclassical approach neglects any tunnelling effect, which could assist the charge transfer when vibrational modes of the initial and final states overlap. Under these conditions, the CT occurs at a transition of the energy parabolas of the initial and final states. The activation energy, $\Delta G^*$, also named activation Gibbs free energy in equations (3) and (4), corresponds on the diagram to the energy difference between the bottom of initial state and the transition state. In SI-Figure 19, this energy difference has been marked ellipses for both CS and CR. In the case of the simple dielectric substrate case, CS occurs in the normal region, which implies that the CT state energy parabola crosses the $S_0$ state energy parabola at a higher energy than the minimum of $S_1$. With the same substrate, CR occurs near the barrierless point, so that the $S_0$ state energy parabola crosses the CT state energy parabola near its lowest energy point, which satisfies equation (26)

$$
\Delta G_{\text{CR}}^{Al_2O_3} \approx 0 \quad \text{and} \quad |\Delta G_{\text{CR}}^{Al_2O_3}| \approx \lambda
$$

From the experimental transient data, we know that both CT characteristic times increase, i.e. both rates increases when the dyad molecules are spincoated on HMM substrates. This suggests that for both CS and CR, $\Delta G^*$ increases. Moving the CT energy parabola to the left, i.e. closer to the minima of $S_0$ and $S_1$, would decrease $\Delta G_{\text{CS}}^*$, which would also be achieved by moving CT downwards to lower energy. Neither of these results are consistent with the slower dynamics we measured. Moving the CT energy parabola to the right, i.e. further away from the minima of $S_0$ and $S_1$, would increase both $\Delta G_{\text{CS}}^*$ but would send CR in the normal region, 19,47 which is not consistent with the model as the $\Delta F$ quadratic variation is indeed associated with CR located near the barrierless point in the inverted region.

The only remaining option, to increase both $\Delta G_{\text{CT}}^*$ and keep CR in the inverted region, is to move the CT energy parabola upwards. This is illustrated by the CT$_{\text{HMM}}$ curve in SI-Figure 19 and does not affect the reorganisation energy. As a consequence only a description including an upwards shift of the CT parabola is physically acceptable and consistent with the slowowdown of the CT dynamics herein reported. We also note that a energy parabola representation, such as in SI-Figure 19, has some limitations. Indeed, a shift upwards of the CT parabola could lead to slight variations of measurable parameters such as CT photoluminescence, i.e. a radiative transition from CT$_{\text{HMM}}$ to $S_n$, or photoelectron spectra of D-A layers spincoated on HMM substrates. However, the dyad films show no photoluminescence, which is fully quenched, and is not suitable for CT emission spectroscopy measurements. Time resolved photoluminescence spectroscopy (TRPES) could also be used, 46,69 however, the dyad thin films contain a large fraction of insulating alkyl chains so that the D-A layers deposited on either fused silica or HMM do not present the sufficient conductivity and charging effects are unavoidable. Furthermore, to avoid TRPES data analysis complications, the surface cleanliness is critical and the samples are most often prepared by cleaving or evaporating the samples inside vacuum chamber at high vacuum of typical $10^{-11}$ Torr. In contrast, the dyad films are prepared by spin-coating and cannot be prepared by cleaving or UVH vaporization. Furthermore, the simplified schematic does not include vibronic states, 36 which for instance possible alterations by the HMM substrates go beyond the scope of the present study. This limits the scope for predicting a measureable shift of the CT$_{\text{HMM}}$-$S_n$ transition with the materials used in the present study. However, such predictions go beyond the scope of the present manuscript which focuses on original opportunities to control CT dynamics with HMM substrates. Interesting prospects appears in terms of opportunities to explore the potentials of HMMs to control CT states beyond their formation and disappearance dynamics. These are being explored, for instance in a distinct system presenting measurable CT photoluminescence signal which can be used to confirm experimentally the existence of a shift of the CT energy parabola under the influence of non-local effect resulting from the HMM structure as it is suggested by the numerical assessment of the stabilisation energy based on our theoretical development. 34

SI-VII. Glossary

- $\alpha$: thickness of the metal and dielectric layer in the HMM, i.e. half of the HMM period.
- $b = a / d$: normalised dipole length-HMM thickness layer.
- $d$: dyad dipole length.
- $f_m$: metal volume fraction in the HMMs.
- $f_d$: thickness of the alkyl melt separating the donor and acceptor columns from the $\text{Al}_2\text{O}_3$ top interface of the substrates as measured by GIXAWS.
- $L$: thickness of the dyad film as measured by Dektak.
- $p$: number of metal dielectric pairs in the HMM substrates.
- $\rho$: dipole vector.
- $q_{DA}$: the atomic charges of the donor and the acceptor.
- $r = z / d$: normalized dipole-HMM interface distance.
- $R_{CC}$: center-to-center distance between the donor and the acceptor.
- $R_{D/A}$: the separation of the donor and the acceptor.
- $r_{D/A}^0$: the ionic radius of the donor and the acceptor with $2|r_{D}^0| = 1/|r_{A}^0| + 1/|r_{A}^-|$.
- $t_m$: thickness of the metal and dielectric in an HMM structure.
$\varepsilon$ : distance from the top interface of the substrate to the dipole.

$\varepsilon_{\text{eff}}$ : dielectric permittivity of the environment (solvent or matrix).

$\varepsilon_{\text{D}}$ : non-local dielectric permittivity, including image dipole interactions resulting from the dipoles located nearby the HMM structure.

$\varepsilon_m$ : permittivity of the metal.

$\varepsilon_d$ : permittivity of the dielectric.

$\Delta \varepsilon_{\text{xx-zz}}$ : xx and zz permittivity of an HMM structure.

$\gamma$ : dipole orientation with respect to metal interface parallel ($\gamma = 1$), perpendicular ($\gamma = 0$), and isotropic ($\gamma = 2/3$).

SI-VIII. References


43. Messina, F., et al., Real-time observation of the charge transfer to solvent dynamics. 4, 2119 (2013).