

Charge transfer enhanced annihilation leading to deterministic single photon emission in rigid perylene end-capped polyphenylenes.

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Synthesis of 1 and 2: Dibromopentaphenylene **1** and perylene boronate ester **2** were synthesized according to literature.[1]

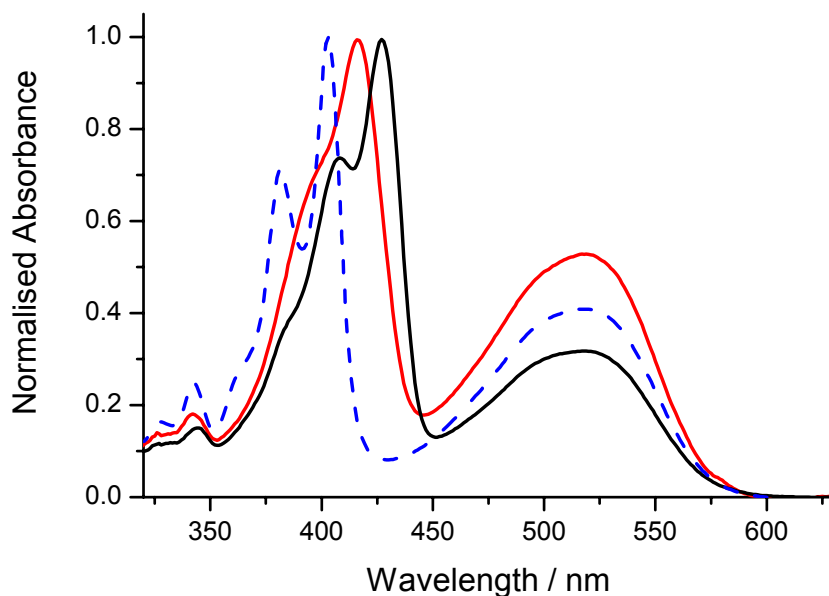
Synthesis of 3: Dibromopentaphenylene **1** (1.65 g, 0.92 mmol) boronate ester **2** (0.28 g, 0.46 mmol) K₂CO₃ (126 mg, 0.92 mmol) THF (24 mL) H₂O (6 mL) were taken in a 100 mL schlenk flask and purged with argon for 20 minutes. To this, tetrakis(triphenylphosphine)palladium (0) (10.6 mg, 9.2 μmol) is added and heated at 85 °C for 16 hours. The product is extracted into dichloromethane, washed with brine and dried over MgSO₄. The crude is loaded on silica and chromatographed using 0-5 % ethyl acetate in hexane as eluent. Isolated yield of **3** = 523 mg (52 %). ¹H NMR: δ 8.62 (2H, dd, J = 8.2, 1.3 Hz) 8.44 (4H, m) 8.11 (1H, d, J = 8.5 Hz) 7.92-7.70 (8H, m) 7.59-7.16 (25H, m) 2.84 (2H, septet, J = 6.6 Hz) 2.63 (8H, t, J = 8.8 Hz) 2.12 (8H, m) 1.65 (8H, m) 1.45-1.05 (92H, m) 0.91-0.70 (m, 32H). FDMS: m/z 2191.70 Elemental Analysis: Calculated C 85.51 H 8.74 N 0.64 Found C 86.40 H 8.73 N 0.66

Synthesis of the boronate ester 4: The monobromide **3** (0.25 g, 0.11 mmol) Bis-(pinacolato)-dibor (35 mg, 0.13 mmol) potassium acetate (34 mg, 0.34 mmol) (diphenylphosphinoferrocenyl)palladium dichloride (1.7 mg, 2.28 μmol) and are taken in 4 mL of dioxane and heated under argon at 85 °C for 36 hours. The reaction crude is loaded on silica and chromatographed using 0-10 % ethyl acetate in hexane as eluent. Isolated yield of **4** = 156 mg (61 %). ¹H NMR: δ 8.65 (2H, d, J = 7.9 Hz) 8.58-8.49 (4H, m) 8.10 (1H, d, J = 8.5 Hz) 7.88-7.50 (15H, m) 7.39-7.13 (18H, m) 2.80 (2H, septet, J = 6.6 Hz) 2.60 (8H, t, J = 9.1 Hz) 2.10 (8H, m) 1.62 (8H, m) 1.38-1.09 (104H, m) 0.91-0.63 (32H, m). FDMS: m/z 2240.60 Elemental Analysis: Calculated: C 86.93 H 9.10 N 0.63 Found C 87.07 H 9.03 N 0.66

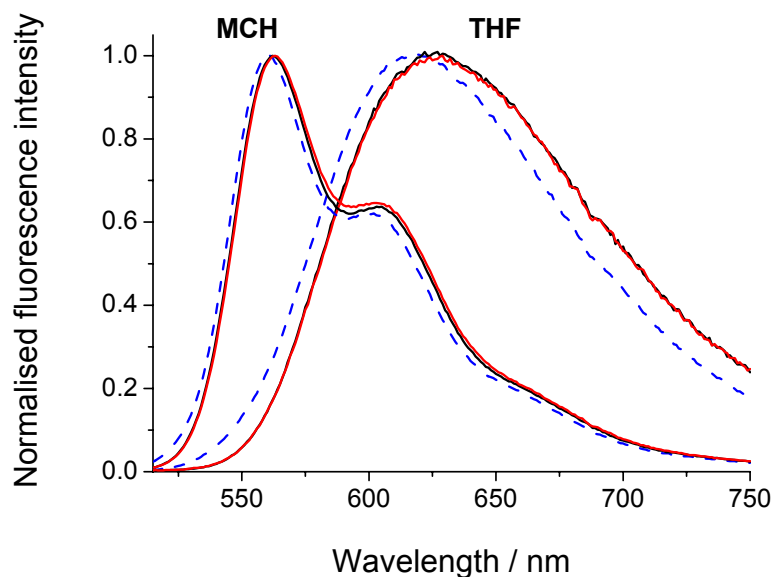
Synthesis of 6: The monobromide **3** (40 mg, 18.2 μmol) boronate ester **4** (41 mg, 18.3 μmol) K_2CO_3 (5 mg, 36 μmol) are taken in a schlenk flask containing 4 mL of THF and 1 mL of H_2O . This is purged with argon for 15 minutes and then tetrakis(triphenylphosphine)palladium(0) (0.8 mg, 0.68 μmol) is added and heated for 48 hours at 85 °C. The crude is then chromatographed on silica using 0-10 % ethyl acetate in hexane as eluent. Isolated yield of **6** = 63 mg (82 %). ^1H NMR: δ 8.65 (4H, d, $J = 7.5$ Hz) 8.51 (8H, m) 8.10 (2H, d, $J = 8.5$ Hz) 7.90-7.50 (30H, m) 7.40-7.31 (20H, m) 7.20-7.16 (16H, m) 2.81 (4H, septet, $J = 6.9$ Hz) 2.61 (16H, t, $J = 7.1$ Hz) 2.13 (16H, m) 1.61 (16H, m) 1.42-1.15 (184H, m) 0.91-0.78 (64H, m). MALDI-TOF: m/z 4223 Elemental Analysis: Calculated C 88.75 H 9.07 N 0.66 Found C 88.64 H 9.18 N 0.71

Synthesis of 7: The boronate ester **4** (40 mg, 17.9 μmol) dibromide **1** (15.2 mg, 8.5 μmol) K_2CO_3 (2.4 mg, 17.3 μmol) are taken in a schlenk flask along with 4 mL of THF and 0.5 mL of H_2O . This is purged with argon for 20 minutes and then tetrakis(triphenylphosphine)palladium(0) (0.4 mg, 0.35 μmol) was added and heated at 85 °C for 48 hours. The crude is then chromatographed on silica using 0-5 % ethyl acetate in hexane as eluent. Isolated yield of **7** = 23.0 mg (46 %). ^1H NMR: δ 8.67 (4H, d, $J = 7.6$ Hz) 8.57 (8H, m) 8.10 (2H, d, $J = 8.5$ Hz) 7.87-7.48 (42H, m) 7.38-7.13 (52H, m) 2.77 (4H, septet, $J = 6.7$ Hz) 2.60 (24H, t, $J = 8.2$ Hz) 2.10 (24H, m) 1.62 (24H, m) 1.43-0.76 (360H, m). MALDI-TOF: m/z 5854 Elemental Analysis: Calculated C 89.06 H 9.37 N 0.48 Found C 89.07 H 9.42 N 0.53

Steady state spectra: Absorption spectra (SI Figure 1) of **6** and **7** are similar to the model compound **3-ph**. The maximum of the pPh absorption is further red-shifted as the number of pPh units increases indicating that they are strongly coupled to each other allowing excitation energy to delocalise. Fluorescence emission spectra (SI Figure 2) in MCH are characteristic of locally excited PI. Emission is always from PI even when excitation is into the pPh absorption band indicating that efficient energy funnelling from the pPh groups to the lower energy PIs takes place before emission occurs. The emission for **6** and **7** is red shifted and loses structure in THF compared to MCH indicating that the emissive state is now a CT state rather than the locally excited PI and is a little further red shifted with respect to **3-ph** indicating that the CT states of **6** and **7** are lower in energy by 2.5 kJ/mol.



SI Figure 1. Absorption spectra in THF of **6** (solid red line) and **7** (solid black line) and of **3-ph** in (dashed blue line) for comparison. Spectra have been normalised to 1.0 at the pPh maxima.



SI Figure 2. Steady state corrected emission spectra in MCH and THF for **3-ph** (dashed blue lines), **6** (red lines) and **7** (black lines). Emission spectra are all normalised to 1.0 at the emission maxima. The loss of structure and broadening of emission is due to a change in the nature of the emissive state from LE to CT on increasing polarity of the solvent.

Calculation of spectral overlap integrals: Spectral overlap integrals, J , were calculated from

$$J(\tilde{\nu}) = \int_0^{\infty} \frac{f_D(\tilde{\nu})\varepsilon_A(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu} \quad (\text{S1})$$

where $\tilde{\nu}$ indicates units of wavenumbers, ε_A is the molar extinction coefficient of the acceptor at a given wavenumber and $f_D(\tilde{\nu})$ is the normalised fluorescence spectrum of the donor with the area under the emission spectrum plotted in wavenumbers being equal to 1.

Fluorescence spectra of **6** and **7** in MCH and THF were considered to be representative of pure LE and pure CT emission, respectively, and the excited state $S_I \rightarrow S_n$ absorption of PI and excited state CT absorption of PI^- and pPh^{++} were estimated from femtosecond transient absorption spectra of **3-ph** recorded in MCH and benzonitrile, respectively. (See below).

Critical distances were calculated from,

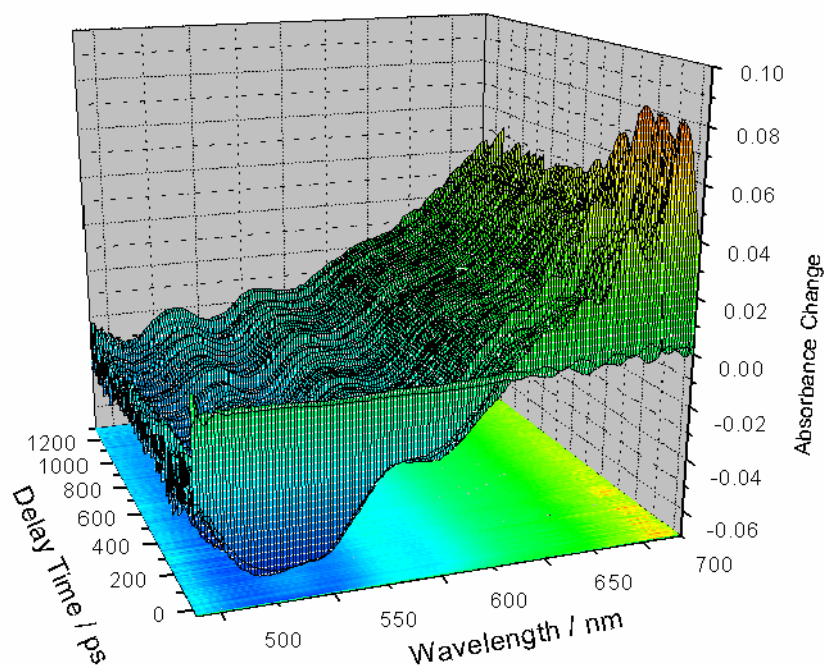
$$(R_o)^6 = \frac{9000(\ln 10)\kappa^2\Phi_D J(\tilde{\nu})}{128\pi^5 N_A \eta^4} \quad (\text{S2})$$

where Φ_D is the fluorescence quantum yield of the donor, N_A is Avagadro's number, κ^2 is the orientation factor, η is the solvent refractive index and $J(\tilde{\nu})$ is the spectral overlap integral of the fluorescence emission spectrum of the donor with the relevant absorption spectrum ($S_I \rightarrow S_n$ or CT) of the acceptor as defined above.

Φ_D of both LE and CT in PMMA were assumed to be 0.7 on the basis of Φ 's measured in solvents of polarity close to that of PMMA and that SM studies[2] on **3-ph** showed that the count rate (i.e. Φ) of SMs did not alter noticeably when emission spectra changed from LE-like to CT-like. ε_A was calculated at each wavenumber based on a value of $40000 \text{ mol}^{-1}\text{cm}^{-1}$ at the maximum absorption of the PI band.[3] This method is only a first approximation and is likely to have considerable error associated with it. It should be pointed out, however, that even if the error in the values of ε_A used for the excited states are $\pm 20\%$, this leads only to an error in R_o of $\pm 3\%$ due to the 1/6 power dependence of R_o on J . The refractive indexes of MCH and THF were used for LE and CT calculations as the emission spectra used were recorded in these solvents.

For the calculation of rate constants and efficiencies of annihilation, k_{ann} and E_{ann} , centre-to-centre distances and κ^2 were obtained from structures computed by molecular mechanics using the Merck force field as implemented in SPARTAN02 (Wavefunction Inc., Irvine, CA). These calculations show that the pentaphenyl groups are quite linear and rigid and that as a result, the transition dipoles of the PIs, which are oriented along the long axis of the chromophore, only deviate from a linear alignment by 2 – 3 degrees, thus $\kappa^2 = 4.0$. Based on SM results [2] on **3-ph**, values of fluorescence decay time of the LE and CT states in PMMA of 3.0 and 2.7 ns, respectively, were used.

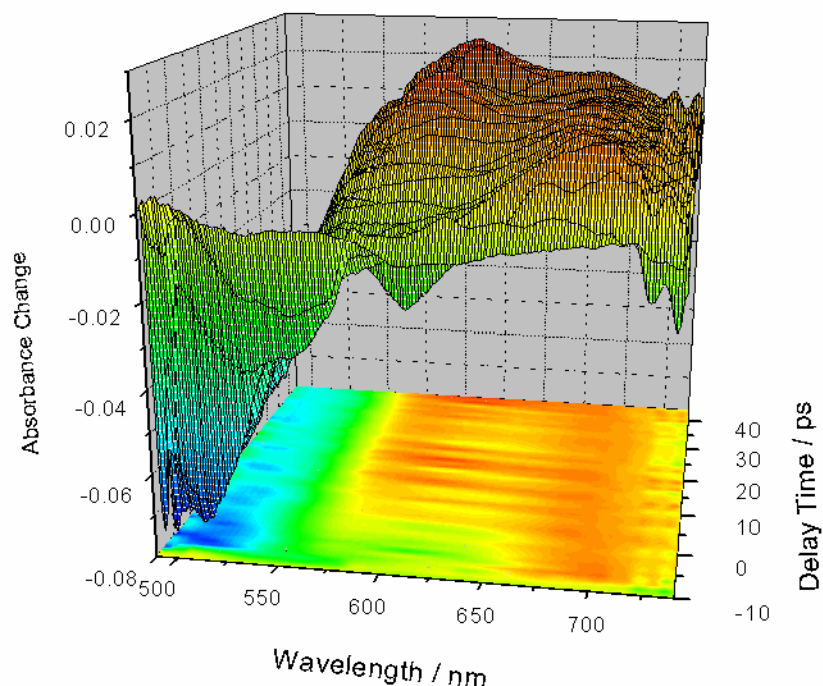
Femtosecond transient absorption spectra of 3-ph: In MCH (Figure 3) there is no formation of CT state and the $S_1 \rightarrow S_n$ absorption of PI is visible as the positive absorption band centred around 710 nm which is similar to that for the related PI-polyfluorene compounds studied previously. [4] The negative band in the shorter wavelength area at 520 nm is due to bleaching of the ground state (GS) absorption of the PI chromophore and there is also a negative contribution to the transient spectrum from stimulated emission in the region of ~530 – 700 nm.



SI Figure 3. Femtosecond transient absorption spectra of **3-ph** in MCH. The increase in the delay time between the pump and probe pulses for successive spectra is 2.73ps. The negative

absorption band around 500 nm is due to depletion of the ground state absorption of the PI chromophore while the positive absorption band at 700 nm is due to $S_I \rightarrow S_n$ absorption by PI. The magnitude of the GS depletion band was used to estimate the molar absorptivity coefficient of the $S_I \rightarrow S_n$ absorption by simple comparison at their respective maxima as there is minimal contribution from stimulated emission at both wavelengths. Taking $\epsilon_{(GS)}$ for PI as $40000 \text{ mol}^{-1}\text{cm}^{-1}$, [3] yielded a value for ϵ_A for $S_I \rightarrow S_n$ of $50000 \text{ mol}^{-1}\text{cm}^{-1}$.

In benzonitrile, formation of $\text{PI}^{\bullet-}$ and $\text{pPh}^{\bullet+}$ can be seen in the longer wavelength part of the spectrum clearly growing in over the first 10 – 20 ps, following the initial, very rapid appearance of $S_I \rightarrow S_n$ absorption (Figure 4). The excited CT state absorption is similar to the previously published spectrum of **3-ph** in THF, [2] however, in benzonitrile, there is no complicating negative contribution to the spectrum from stimulated emission as the CT state recombines non-radiatively in this solvent, ($\Phi < 5\%$). Again, the extent of the GS depletion band at 520 nm can be used to estimate the molar absorptivity coefficient by direct comparison yielding an ϵ_A for $S_{I(CT)} \rightarrow S_{n(CT)}$ of $20000 \text{ mol}^{-1}\text{cm}^{-1}$.



SI Figure 4. Femtosecond transient absorption spectra of **3-ph** in benzonitrile. The increase in the delay time between the pump and probe pulses for successive spectra is 1.0 ps. The negative absorption band around 520 nm is due to depletion of the ground state absorption of the PI chromophore. In the longer wavelength area of the spectrum, at short delay times, there is a positive absorption band at 700 nm due to $S_I \rightarrow S_n$ absorption by PI while at longer delay

times the absorption is much broader and is due to PI^- and pPh^{*+} . The grow-in of these species over the first 10-20 ps can be seen clearly between 600 and 650 nm.

References

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