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

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Two new peryleneimide end-capped polyphenylenes are shown to be deterministic single photon sources in PMMA films due to efficient annihilation between charge transfer states.

The synthesis and photophysical characterisation of conjugated organic oligomers and polymers have attracted much attention in recent years due to their potential for use as active materials in OLEDs,[1,2] photovoltaic devices,[3] plastic lasers[4] and field effect transistors.[5] Of particular recent interest, primarily due to their potential as blue-emitting materials in LEDs and plastic lasers, are polymers containing phenylene-based moieties such as poly-fluorenes,[6] polyindenofluorenes[7,8] and ladder-type poly-*p*-phenyl-enes.[9] Recently, we reported the synthesis[10] of a new rigid ladder-type pentaphenylene **1** and well-defined oligomers derived from it.[11] The pentaphenylene unit (pPh) is interesting in that its polymers are stable blue light emitters. Furthermore, pPh can be readily functionalised with chromophores, for example, perylene imide (PI), in order to tune this emission across the visible range. The potentially broad range of applications for molecules and oligomers based on these units was highlighted very recently by us when we observed that the emissive state of a PI–pPh molecule (labelled **3-ph** here; *i.e.* molecule **3** in Scheme 1 but with the Br replaced by a phenyl group) switches from the locally excited (LE) singlet state of PI to a charge transfer (CT) state on a mild increase in the environment polarity.[12] This phenomenon was observable at the single molecule (SM) level in a PMMA film demonstrating the potential for the use of this molecule as a highly sensitive polarity probe. Recent quantum chemical calculations by Sun[13] on a slightly simplified version of this molecule concur with our interpretation of these spectral changes with polarity being due to the emissive state changing from LE to CT in nature.

There is also currently much interest in developing room-temperature single photon (SP) sources driven mainly by potential applications in quantum computing and quantum cryptography.[14] In another recent study of ours,[15] a series of molecules where two

PIs are separated by a number (3, 6 or ~42) of fluorene moieties, the two shorter systems were shown to be efficient SP sources at room temperature. Pentaphenyl moieties are also attractive spacers for separating two PI units as the pPh building blocks are each about two nanometers long, quite rigid and linear. However, as our previous studies have shown,[10,12] these units are not simple spacers but can be involved directly in the photophysics *via* charge separation processes with a suitable acceptor. We now report the synthesis of two rigid, extended PI end-capped systems **6** and **7** with two and three pPh moieties between the PIs, respectively, and the results of photon anti-bunching measurements on single molecules embedded in PMMA films which show that both systems are highly efficient, deterministic SP sources at room temperature. Furthermore, we show that this phenomenon is due to annihilation processes involving two CT states and calculations indicate that this leads to a considerable enhancement in the annihilation efficiency compared to between two LE states.

The key to the synthesis reported here is the isolation of **3**, a pentaphenylene bearing perylene monoimide at one end and bromine at the other. This can be further suitably functionalised to generate **4**, another valuable synthon as shown in Scheme 1.

Reaction of perylene boronate ester **2** with a two-fold excess of **1** in a Suzuki-type coupling generated the hetero functionalised pentaphenylene **3** in 52% isolated yield. A small amount of the dicoupled product is also formed in the reaction, however, it is
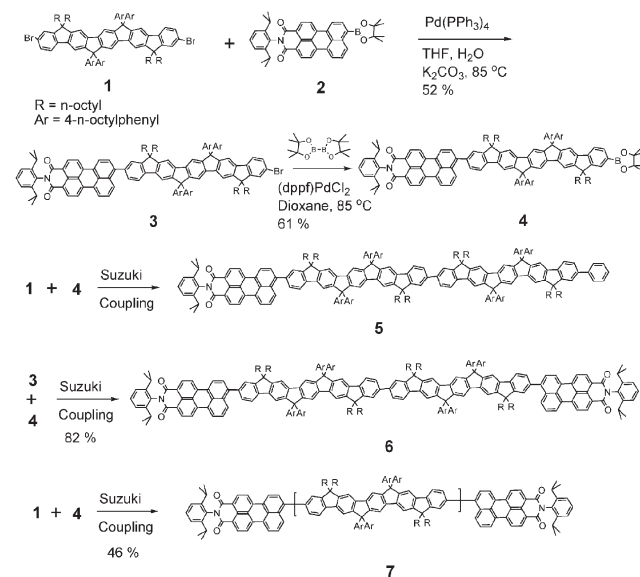
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Scheme 1

completely separable from the desired product. **3** is converted to the corresponding boronate ester **4** in a palladium catalysed reaction using bis(pinacolato)diboron in 61% yield. Suzuki coupling of **3** and **4** generated a dimer of pentaphenylene **6** end-capped with PI at either end. Analogous coupling of **1** with **4** afforded a trimer of pentaphenylene **7** end-capped with PI in 46% yield. All compounds were characterised by NMR, MALDI-TOF and elemental analysis. For the synthesis of **5**, **4** was treated with a two-fold excess of **1** in a Suzuki-type coupling followed by the addition of phenylboronic acid for end-capping. However, in this case, the desired product **5** was isolated only in 60–65% purity, the contaminant containing only one pentaphenylene group, *i.e.*, compound **3-ph** (see ESI†).

While a full photophysical study at both the ensemble and single molecule study will be reported separately, one interesting result is that both molecules act as deterministic single photon (SP) sources at room temperature, emitting only one photon when both PIs are excited by a single laser pulse. Fig. 1 shows a fluorescence trajectory from a single molecule of **7** embedded in a PMMA film. Films were deposited by spin-casting (60 s @ 1200 rpm) onto thoroughly cleaned coverslips from $\sim$5 mg ml^{-1} solutions of PMMA (Aldrich, T_g = 122 °C, M_w = 350 000) in CHCl$_3$ (Aldrich, spectroscopic grade) containing $\sim$10^{-10} M **6** or **7**. SMs were excited by sufficiently intense laser pulses ($\sim$3 kW cm^{-2}) to ensure a significant probability of both PIs absorbing a photon. The laser source was a mode-locked regeneratively amplified Ti:Sapphire laser (Spectra Physics) giving 488 nm light at 8.18 MHz with a fwhm of 1.2 ps. Fluorescence photons were detected by two avalanche photodiodes in a classical Hanbury-Twiss and Brown[16] set-up. Full details of the SM detection set-up are published elsewhere.[17]

The trajectory in Fig. 1 shows two clear intensity levels indicative of stepwise irreversible photobleaching of the two PI chromophores. Analysis of the interphoton arrival times for the first level (where both PIs are not yet photobleached and can absorb photons) yields the coincidence plot shown in the inset to Fig. 1. The lack of a central peak at interphoton times around zero is indicative of a single emitter; for two emitters, the central peak is expected to be half the size of the lateral peaks.[18,19] There is a small number of counts in the central peak due to background scattered photons. The ratio of the central peak to the average of the lateral peaks, N_C/N_L, calculated for the whole of the first intensity level is 0.07 and as can be seen by the plot in Fig. 1, where this ratio is calculated every 50 000 photons, it does not vary much around this value.
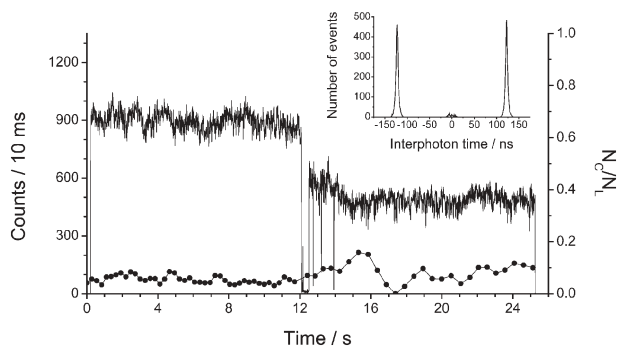
Fig. 1 Fluorescence trajectory and N_C/N_L ratio calculated every 50 000 photons for a single molecule of **7** in PMMA. Inset: Interphoton time distribution for the entire higher intensity level of the trace.
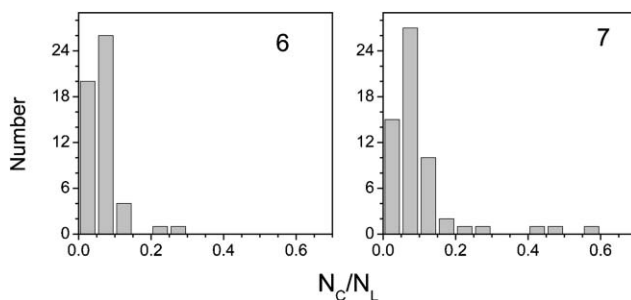
Fig. 2 Histograms of N_C/N_L values for single molecules of **6** and **7** in PMMA. Only molecules that showed two clear intensity levels are included and N_C/N_L values are calculated from the whole of the first level.

Histograms of average N_C/N_L values for 52 molecules of **6** and 59 molecules of **7** in PMMA are shown in Fig. 2. Only molecules showing two clear intensity levels like the example shown in Fig. 1 were included and the average N_C/N_L value was determined from analysis of the whole of the higher intensity level. For **6**, 50 out of 52 molecules (96%) have N_C/N_L values less than 0.2 and of these, 46 molecules (88%) are lower than 0.1. This is a good indication that **6** acts as a SP source under these conditions. For **7**, the statistics are not quite as good but still show that **7** is quite an efficient SP source with 54 out of 59 molecules analysed showing a N_C/N_L value below 0.2 and of these, 42 (71%) are below 0.1. Three molecules of **7** showed N_C/N_L values close to 0.5, this being indicative of two photons being emitted.

The observation of SP emission at room temperature from molecules such as these is normally due to highly efficient singlet-singlet (SS) annihilation being operative.[15,20,21] In this process, the excited singlet state (S$_1$) on one PI transfers its energy to the other and returns to the ground state while the second PI is promoted to a higher excited state (S$_n$) and then returns rapidly to S$_1$ *via* vibrational relaxation with the net result being the loss of one of the two excited states. SS annihilation is a resonant energy transfer process and can be described by the well known Förster formulism for dipole–dipole resonant energy transfer[22] which depends primarily on the orientation of the two chromophores (expressed in the orientation factor, κ^2), the fluorescence quantum yield of the donor, Φ_D, and the spectral overlap, J, of this fluorescence with the ground state absorption of the acceptor. For SS annihilation, the spectral overlap integral is now calculated from the excited state (S$_1$ $\rightarrow$ S$_n$) absorption spectrum of the acceptor and the fluorescence spectrum of the donor. A critical distance, R_0, for this process, where the rate constant for SS annihilation, k_{ann}, is such that the probability of SS annihilation occurring is 50%, can be defined,

$$k_{ann} = \tau_D^{-1}/(R_0/R_c)^6 \qquad (1)$$

where τ_D is the fluorescence lifetime of the donor in the absence of an acceptor and R_c is the chromophore separation. The efficiency of annihilation, E_{ann}, can then be defined as,

$$E_{ann} = R_0^6/(R_0^6 + R_c^6) \qquad (2)$$

Table 1 gives calculated values of J, R_0, k_{ann} and E_{ann} for both annihilation between two LE states and two CT states. Details of the calculations are given in the ESI.† It is clear that for **7**, due to

Table 1 Calculated chromophore separations, overlap integrals, critical distances, rate constants and efficiencies of annihilation for **6** and **7**

	R_c	$10^{13}J$	R_0	$10^{-9}k_{ann}$	E_{ann}
6-LE	53	0.97	63	0.92	73
7-LE	74	0.99	63	0.13	27
6-CT	33	2.58	73	44.5	99
7-CT	54	2.59	73	2.32	86

R_c and R_0 are in Å, J is in cm^{-6} mol^{-1}, k_{ann} is in s^{-1} and E_{ann} is in %.
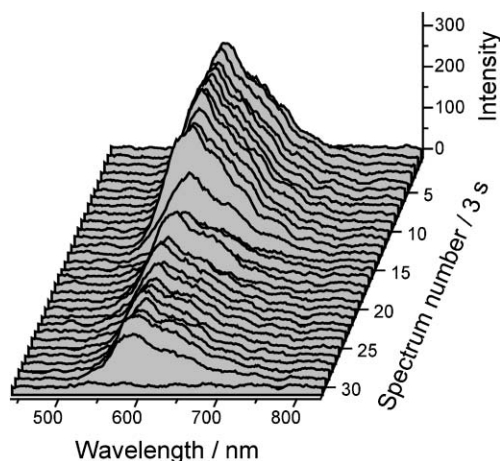
Fig. 3 Emission spectra from a SM of **7** embedded in PMMA. Spectra were recorded every three seconds.

the efficiency of SS annihilation between LE states being quite low (27%), this system should not be an efficient SP source if annihilation involves LE states. For **3-ph** in PMMA, 65% of the SMs studied showed CT-like spectra for at least part of their fluorescence trajectory[12] and SM spectral studies show that **7** also forms CT states in PMMA with similar statistics. An example of emission spectra from a SM of **7** in PMMA recorded using a liquid N_2 cooled CCD camera (Princeton), is shown in Fig. 3. The spectra are quite CT-like, particularly in the higher intensity region at early times where two PIs are absorbing and emission maxima are around 595 nm. (See the ESI† for steady state fluorescence spectra of **7**.) It can be concluded that annihilation between two CT states is occurring for these molecules.

Involvement of the CT state in an annihilation process is allowed within the Förster formulism as long as there is no change in the electron spin during the acceptor transition. J_{CT} is almost three times larger but this only translates into a 15% increase in R_0 which ordinarily would not lead to sufficient increases in k_{ann} and E_{ann} to account for the experimental observations. Another consequence of annihilation occurring between two CT states is, however, that the effective distance between the donor and acceptor chromophores would be much shorter as the CT state involves both a PI and a pPh. For **6** and **7**, when both PIs are excited and form CT states with adjacent pPh units, the centre-to-centre distance is effectively reduced by the length of one pPh unit or 2 nm. The values of k_{ann} calculated taking this into account are fast enough to lead to completely effective annihilation in **6** (E_{ann} = 99%) and very efficient annihilation in **7** (E_{ann} = 86%).

These CT based efficiencies are in agreement with the SM antibunching data further indicating that CT states are, indeed, involved. The three molecules of **7** which showed N_C/N_L values around 0.5 could be molecules which are in nano-environments non-polar enough that the molecules only formed LE states during their trajectories. This is in line with the large difference between E_{ann} for LE and CT based annihilation for **7** which predicts that **7** should be a single emitter when it can form CT states and a dual emitter when it forms only LE states. This opens up the intriguing possibility of environmental control of the annihilation process (and thus the nature of the deterministic emission) for this molecule by switching of the emissive state between the LE and CT states. Such switching could be achieved, for instance, by an externally applied electric field.

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