

# Fluorescence quenching and enhancement of vitrifiable oligofluorenes end-capped with tetraphenylethene<sup>†</sup>

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We report the synthesis of novel amorphous fluorene-based fluorophores that have been end-capped with tetraphenylethene (TPE). Although in the solid state the fluorophores show bright cyan fluorescence with high (68%) photoluminescence quantum efficiency (PLOE), strong fluorescence quenching is observed in solution with low PLQE values ranging from 0.3% to 2.1%. When the fluorophores were added to a 90% water-THF solvent mixture nanoparticles were formed, which was confirmed by Dynamic Light Scattering (DLS) and Atomic Force Microscopy (AFM). Subsequent fluorescence measurements reveal that all the fluorophores exhibit aggregation induced emission (AIE) with high PLQE (41%). We have carried out a comparative study of 5 fluorene-based TPE materials (F(1-5)TPE), in which the fluorene core is extended, and investigated their thermal, optical, electrochemical and electroluminescence properties. From fluorescence quantum yield data we have discovered that the AIE effect decreases as the fluorene core increases both in the nanoparticle and in the solid state. Thermal analysis reveals that all fluorophores are amorphous with high thermal stabilities. Potential application in solid state vapour sensing has been demonstrated using dichloromethane that shows "on" and "off" fluorescence behaviour. Finally, Organic Light Emitting Diodes (OLEDs) have been fabricated with device configuration ITO/PEDOT/F(1-5)TPE/TPBi/LiF/ Al. The best OLED device that incorporates F1-TPE as the emitter exhibits a turn-on voltage of 5.8 V,  $L_{\text{max}} = 1300 \text{ cd } \text{m}^{-2}, \, \eta_{\text{P,max}} = 1 \text{ lm } \text{W}^{-1} \text{ and } \eta_{\text{C,max}} = 2.6 \text{ cd } \text{A}^{-1}.$ 

# Introduction

Fluorene has attracted interest for many years in academia and industry for applications in electronics and optoelectronics, such as OLEDs, Organic Field-Effect Transistors (OFETs) and solar cells.<sup>1</sup> Its near planar biphenyl unit ensures a high degree of conjugation and its synthetic versatility at the benzylic 9-position and aromatic 2,7-positions allows ease of design and synthesis. Polyfluorenes (PFs) and their co-polymers have become a major class of solution processable organic semiconductors and display high fluorescence quantum yields in solution and solid state, good solubility, high charge-carrier mobilities and high thermal

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stability. PF homopolymers also exhibit thermotropic liquid crystallinity<sup>2</sup> and can be aligned on rubbed polyimide resulting in polarised light emission with a polarisation of 15.<sup>3</sup> In contrast to PF, oligofluorenes exhibit monodispersity and improved chemical purity. Due to their linear structures and high aspect ratios oligofluorenes and fluorene-based low molecular weight materials have been reported to exhibit smectic and glassy nematic liquid crystalline states.<sup>4</sup> Also, aligned thin films have been reported to exhibit linearly<sup>5</sup> and circularly polarised light emission<sup>6</sup> and high field-effect mobilities.<sup>7</sup> Additionally, oligofluorenes show attractive properties for cholesteric liquid crystal lasers.<sup>8</sup> Vitrification above room temperature is a very important prerequisite for certain optoelectronic applications, and both oligofluorene and polyfluorene can form high quality thin glassy films without crystal grain boundaries.

Aggregation induced emission (AIE) was discovered in 2001,<sup>9</sup> and within the last few years a great deal of effort has been undertaken to study this phenomenon. AIE-active materials are chromophores that exhibit quenching in the solution, contrary to its solid (or "aggregated") state, which shows luminescence. This is opposite to aggregation caused quenching (ACQ), which demonstrates larger quantum efficiencies in solution compared to its solid state. Restriction of intramolecular rotation (RIR) is

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a common structural feature of these materials and has been used to explain the AIE phenomenon.<sup>10</sup> In AIE-active materials these low frequency modes have a large influence on the internal conversion and, accordingly, in the solid state they contribute less to the internal conversion resulting in the prevalence of radiative decay.<sup>11</sup> In the non-aggregated state the light emission is turned "off", opposite to its aggregated state that turns "on" the light emission. This "on-off" fluorescence behaviour is important for sensing applications. Due to these novel and attractive properties, AIE-active materials have found widespread applications, ranging from chemosenors,12 fluorescent assays,13 solvent vapour/explosive sensors,14 OLEDs15 and twophoton absorption and excitation.16 The most common class of materials reported in the literature that exhibit AIE properties and have been researched for such applications incorporate silole17 and TPE18 groups. However, the majority of these previously reported materials tend to be non-linear in structure with a low aspect ratio.

It was our interest to synthesise a material that possesses the attractive properties of oligofluorene, such as high thermal stability, good solution processability and glassy behaviour, which is able to quench its emission in solution but retain the high PLQE and AIE properties of TPE in the solid state. Here, we report the synthesis of a series of amorphous fluorene oligomers (F(1-5)TPE; Fig. 1) that exhibit fluorescence quenching in solution, in contrast to its nanoparticle and solid states that exhibit bright cyan luminescence. A detailed comparative study has been carried out with analogous materials that differ only by the number of fluorene rings in its core. With regards to F5-TPE, the PLQE in solution is reduced from 96% (oligo-5-fluorene, without TPE groups) to 2.1% by simply end-capping with TPE. Solid state amorphous patterns have been fabricated that exhibit "on-off" fluorescence switching when exposed to solvent vapour. Finally, OLEDs have been fabricated with device configuration ITO/PEDOT/F(1-5)TPE/TPBi/LiF/Al.

#### **Results and discussion**

#### Synthesis

The structure of fluorene can be easily functionalised by nucleophilic substitution at the 9-position, due to the acidity of the benzylic protons, and electrophilic substitution at the 2- and 7-positions due to the reactivity of electrophiles with the electron-rich aromatic ring. Long alkyl chains enhance the solubility of extended fluorene oligomers and can effectively increase the viscosity, which is necessary to inhibit crystallisation and encourage glassy behaviour above room temperature. If the alkyl chains are too long at the fluorene 9-position the glass transition temperature ( $T_g$ ) will have a tendency to be lower, and possibly



Fig. 1 Structures of F(1–5)TPE.

below room temperature, compared to shorter alkyl chains.<sup>4a</sup> Indeed, due to the decrease of the van der Waals forces and hence the free volume shorter chains will result in an increase of the  $T_{\rm s}$ , however, at the expense of solubility. Therefore, octyl chains were viewed as a reasonable compromise. F(1-5)TPE were synthesised according to Schemes 1 and 2. A convergent approach was adopted from two different pathways, involving a boronic acid or ester tetraphenvlethene derivative and a brominated fluorene core. Ultimately the Pd(0)-catalysed Suzuki cross coupling was used to perform the end capping. Dialkylation of 1 at the fluorene benzylic 9-position was carried out using the KOH/KI/DMSO method and 1-bromooctane as the alkylating agent. The crude product was purified by recrystallisation using ethanol to give 2 in excellent yield (84.1%). Commercially available 2-bromofluorene was alkylated using the same conditions used to prepare compound 2. Reaction of 3 in dry THF with *n*-BuLi in standard subambient conditions  $(-78 \ ^{\circ}C)$ . followed by quenching using distilled tri(isopropyl)borate and subsequent acidification afforded the boronic acid 4. Bis-fluorene (5) and ter-fluorene (6) were subsequently synthesised by Suzuki cross couplings of compounds 3 and 4 or 2 and 4, respectively, in toluene and water (2:1 ratio). Controlled bromination at the active 2 and 7 positions yielded the dibrominated compounds 7 and 8. Diphenyllithium was easily prepared from diphenylmethane (9) and *n*-BuLi in THF at 0 °C, which was subsequently added to 4-bromobenzophenone and dehydrated using the acid catalyst p-toluenesulfonic acid (PTSA) to give the desired Br-TPE (10). Similar conditions used for the synthesis of compound 4 were followed to make the boronic acid 11. Finally, F(1-3)TPE were prepared by Suzuki cross couplings of the TPEboronic acid 11 and the brominated fluorene cores (2, 7 and 8). A selective Suzuki cross coupling was designed to synthesise the important intermediate 15. Due to the weaker nature of the C-I bond compared to the C-Br bond the coupling reaction at the former should dominate, reducing the amount of di-coupling product. Iodination of 2-bromofluorene (12) using iodine, potassium iodate in acetic acid vielded compound 13 in excellent yield (81.1%). Selective Suzuki cross coupling of compounds 11 and 14 yielded the mono-TPE (15) in good yield (66.1%). This was functionalised with a boronic ester group by reacting with bispinacolatodiboron, KOAc, PdCl<sub>2</sub>(dppf) in dry dioxane to vield the boronic ester (16) in excellent vield (82.7%). Similar Pd(0)-catalysed Suzuki cross coupling protocols were used to synthesise F4-TPE and F5-TPE.

#### Thermal properties

Thermal properties of F(1-5)TPE were evaluated by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). As expected the DSC scans (see Fig. 2) of all 5 fluorophores show a first order transition temperature above room temperature, which represents a glass transition temperature ( $T_g$ ). No crystallisation exotherms are observed on cooling and F(1-5)TPE were isolated as amorphous materials due to the absence of an endothermic melting peak on the first heating cycle. This is probably due to the high viscosity of the amorphous state. All materials exhibit elevated  $T_g$  values compared to the corresponding fluorene-only materials that are not end-capped (see Table 1).<sup>8</sup> Interestingly, for this series of TPE end-capped



Scheme 1 (a)  $C_8H_{17}Br$ , KOH, KI, DMSO, RT, (b) (i) *n*-BuLi (2.5 M), THF (dry), -78 °C, (ii) triisopropylborate, (iii) HCl (20% v/v), (c) Na<sub>2</sub>CO<sub>3</sub> (aq), Pd(PPh<sub>3</sub>)<sub>4</sub>, DME, reflux, (d) Br<sub>2</sub>, DCM (dry), (e) (i) *n*-BuLi (2.5 M), THF (dry), 0 °C, (ii) 4-bromobenzophenone, (iii) PTSA, toluene (Dean–Stark), (f) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene:H<sub>2</sub>O (2 : 1), PTC, 90 °C.

oligo-fluorenes the  $T_g$  values decrease as the fluorene core is extended, therefore, F1-TPE exhibits the largest  $T_{g}$  value (77.0 °C) and F5-TPE exhibits the lowest (55.4 °C). This trend is opposite to the analogous oligo-n-fluorenes, which show an increase in the  $T_{\rm g}$  values as the conjugation length is increased. In this case, if we imagine the molecules sliding past each other in the melt, the molecules without TPE groups can freely slide past each other and exhibit a decrease in the free volume as the conjugation length is increased, and therefore an increase in the  $T_{\rm g}$ . However, after end-capping the rigid and bulky TPE end groups of F(1-5)TPE may obstruct this sliding process decreasing the free volume compared to its fluorene-only analogue, thus exhibiting a comparatively higher  $T_g$  value. From this situation it can be envisaged that the free volume could increase when the fluorene core is elongated because when the fluorene core is large the TPE end groups have less effect on this sliding process and, as a result, the  $T_g$  value decreases. This aforementioned obstruction has a big effect on polymeric materials and generally elevates the  $T_{\rm g}$  value.<sup>20</sup> In any case, this shows that TPE end-capping imposes a strong influence on the thermal properties of the fluorene core and the obstruction of the sliding process might explain why the  $T_{\rm g}$  values of F(2–5)TPE are higher than the oligo-n-fluorenes. All the fluorene-TPE materials form stable glassy films after spin coating from toluene on quartz substrates and no crystallisation is observed for more than 3 months at room temperature. In contrast, oligo-5-fluorene  $(T_{\rm g} = 17 \ ^{\circ}{\rm C})$  spontaneously crystallises by aging at room temperature. High  $T_{\rm g}$  values above room temperature are desirable for uniform and defect-free thin films because they are more likely to stay in their glassy state without crystallisation, which can be detrimental to optoelectronic devices such as OLEDs. The thermal degradation properties of these end-capped TPE fluorenes are also superior compared to the analogous oligo-n-fluorenes (see Table 1). All five materials exhibit negligible differences in  $T_{d}$  values. We have also confirmed the amorphous nature of these materials by XRD analysis (see Fig. 3), in which the diffraction curve shows the characteristic amorphous halo without sharp crystalline diffractions.



Scheme 2 (a) Iodine, potassium iodate, acetic acid,  $H_2O$ , 90 °C, (b)  $C_8H_{17}Br$ , KOH, KI, DMSO, RT, (c)  $K_2CO_3$ , Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene:  $H_2O$  (2 : 1), PTC, 90 °C, (d) bispinacolatodiboron, KOAc, PdCl<sub>2</sub>(dppf), dioxane (dry), 70 °C to 90 °C.



Fig. 2 DSC thermograms showing first-order transitions on the second heating cycle ( $10 \,^{\circ}$ C min<sup>-1</sup>).

# **Optical properties**

#### Steady state UV-VIS absorption and PL emission spectra

The UV-VIS absorption spectra, shown in Fig. 4, shows peaks related to the  $\pi$ - $\pi$ \* transition of the chromophore and demonstrates the influence of conjugation on the maximum absorption wavelength ( $\lambda_{abs}$ ) and molar absorptivity. When the number of fluorene units in the core is enlarged, from F1-TPE to F5-TPE, the  $\pi$ -electron system is increased and the  $\lambda_{abs}$  red shifts in both

 Table 1
 Thermal properties<sup>a</sup>

Material	$T_{\rm g}$ (°C)	$T_{\rm d}$ (°C)		
F1-TPE	77.0	425		
F2-TPE	$68.0 (-20)^8$	$423(374)^8$		
F3-TPE	$65.4(-1)^{8}$	$425(417)^8$		
F4-TPE	$61.4(11)^8$	435 (421) <sup>8</sup>		
F5-TPE	55.4 (17) <sup>19</sup>	429		

<sup>*a*</sup> Abbreviations:  $T_g$  = Glass transition temperature,  $T_d$  = thermal decomposition temperature. For comparison the parentheses denote the values for the analogous fluorene-only materials, oligo-*n*-fluorene (n = 2, 3, 4 and 5).

hexane and THF by 20 nm. Additionally, the molar absorptivity also increases as the degree of conjugation is increased. The increase in the conjugation reduces the optical band gap and, therefore, both bathochromic and hyperchromic shifts in absorption are observed, consistent with the particle-in-a-box model. The absorption spectrum is broad and featureless with no vibrational fine structure, which is common for fluorene-type chromophores. Decreasing the solvent polarity from THF to hexane blue-shifts the  $\lambda_{abs}$  for all the Fn-TPE materials because a less polar solvent can increase the energy of the  $\pi^*$  orbital. However, this is not the case for the emission event (see later).

The  $\lambda_{abs}$  in the solid state (see Table 2) follows a similar trend compared to solution, however, the bandwidth (see Fig. 5) is



**Fig. 3** XRD pattern of the as-synthesised F1-TPE after 6 months of the initial isolation is featureless. The lack of diffraction peaks indicates that F1-TPE remains as an amorphous material for a long period of time without crystallisation.



**Fig. 4** UV-VIS absorption spectra (with molar absorptivity,  $\varepsilon$  in M<sup>-1</sup> cm<sup>-1</sup>) and emission spectra in THF, concentration =  $1 \times 10^{-6}$  M, small peak at 405 nm in the emission spectra for F(1–3)TPE is the Raman peak.

slightly more broadened, perhaps due to the formation of ground state aggregates by interchain  $\pi$ - $\pi$ \* interactions that increases the effective conjugation within the molecule.<sup>21</sup> These

Table 2	Optical	properties'
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oligofluorene-TPE materials exhibit bathochromic shifts in absorption compared to the oligo-*n*-fluorenes that do not incorporate TPE groups, which reflects an increase in the conjugation length due to the TPE end-capping.

Although the magnitude of the Stokes shifts for oligo-n-fluorenes changes very little from the solution to the solid state, the F(1-5)TPE materials exhibit comparatively large changes. The most striking feature of Fig. 4 and Fig. 5 is the large Stokes shifts in the solid state compared to the small Stokes shifts in solution (THF), in which F1-TPE exhibits a Stokes shift of 137 nm (solid state). Provided there is a normal absorption edge, a large Stokes shift means a small overlap between the absorption and emission spectra, which is desirable for optoelectronic applications such as OLEDs, where re-absorption can reduce the device efficiency. In solution oligo-n-fluorenes display small Stokes shifts ranging from 35 nm for oligo-2-fluorene to 41 nm for oligo-5-fluorene, which are similar to the values obtained for our Fn-TPE materials in solution (THF). Conjugated materials favour planar conformations in the excited state compared to the ground state,<sup>22</sup> therefore, these large Stokes shifts in the solid state may be due to conformational changes of the TPE end groups, in which the geometry of the molecule in the ground state is converted to a more planar excited state.<sup>23</sup> Also, the large red-shifts in the PL of the nanoparticle and solid state compared to the solution (THF) suggests that the F(1-5)TPE molecules in solution are more strongly deviated from planarity with a lower degree of conjugation. F5-TPE exhibits a PL<sub>max</sub> of 489 nm in the solid state (thin film) and a  $PL_{max}$  of 413 nm in the solution state (THF) with a calculated red-shift of 76 nm. In comparison, the analogous oligo-5-fluorene shows only a 7 nm red-shift of the PL<sub>max</sub> in the solid state (418 nm, thin film) compared to the solution state (411 nm, THF). In the case of TPE in solution, bond rotational motions are unrestricted, and it is this aspect that results in poor fluorescence quantum efficiencies. Molecular planarisation is more likely to happen in the solution state where molecules are more able to undergo changes in their confirmation. Also, twisted conformations in the ground state usually encourage a planar excited state conformation, *i.e.*, some planar and rigid materials such as ladder type polyparaphenylene are unable to undergo conformational changes in the excited state.<sup>24</sup> Therefore, it appears that the rotational and torsional motions of the TPE end-caps are so excessive in THF solution that planarisation in the excited state becomes so difficult. In the solid state

	<sup>s</sup> λ <sub>abs</sub> (nm)		E .	${}^{s}\lambda_{em} (nm)$			<sup>N</sup> λ <sub>em</sub> (nm)
Fluorophore	Hexane	THF	$^{r}\lambda_{abs}$ (nm)	Hexane	THF	$^{\Gamma}\lambda_{\rm em}$ (nm)	
F1-TPE	353	357	355	525	n.d	492, $492^{b}$	494
F2-TPE	360	365	364	530	n.d	493	498
F3-TPE	367	369	370	535	n.d	488	502
F4-TPE	370	374	372	530	411	489	489
F5-TPE	373	377	374	525	413	489	431 (459, 490)

<sup>*a*</sup> Abbreviations and definitions:  ${}^{s}\lambda_{abs} = maximum$  absorption wavelength in solution (hexane and THF),  ${}^{F}\lambda_{abs} = maximum$  absorption wavelength in film (prepared by spin-casting 0.01 g/0.3 ml from dry toluene solution on quartz substrate),  ${}^{s}\lambda_{em} = maximum$  emission wavelength in solution (hexane and THF),  ${}^{F}\lambda_{em} = maximum$  emission wavelength in film (prepared by spin-casting 0.01 g/0.3 ml from toluene solution on quartz substrate),  ${}^{N}\lambda_{em} = maximum$  emission wavelength in nanoparticle (THF–H<sub>2</sub>O mixture  $f_w = 90\%$ ), all measurements at an excitation of 361 nm, n.d = not detected (fluorescence quenching is observed and the signal is too weak to be accurately determined).  ${}^{b}$  Maximum emission wavelength in powder form.



Fig. 5 The UV-VIS and PL spectra of F(1-5)TPE measured from thin films prepared by spin casting from toluene solution on quartz substrates.

the TPE end-caps are more constrained and rotational motions are more hindered (compared to THF solution), however, its geometry is in fact still non-planar and thus perhaps allows a greater ease for planarisation. The ability of TPE to adopt a large number of interconvertable conformations has been reported previously.<sup>25</sup> Although the emission peaks of F(1-3) TPE in THF solution are not clear due to considerable quenching, with respect to F(4-5)TPE the emission peaks are dominated by the defined vibronic bands of the fluorene core. The PL emission of the fluorophores in hexane seems to be a special case. The absorption maxima of the fluorophores in hexane are blue shifted compared to the absorption maxima in THF. Oppositely, the PL emission profiles for the fluorophores F(1-5)TPE in hexane exhibit huge bathochromic shifts compared to the fluorophores in THF solution. Consequently, the fluorophores exhibit very large Stokes shifts (F1-TPE = 172 nm), which is unusually greater than the Stokes shifts for the solid state. Again, these huge Stokes shifts could be due to a more planar geometry of the molecule in the excited state compared to its ground state. In hexane solution the intramolecular rotations of the TPE end-caps in some of the molecules are more hindered, *i.e.*, they exhibit conformations that are less twisted, compared to the TPE end-caps in THF solution and, therefore, planarisation occurs and red-shifts the PL emission. However, most of the molecules contain more twisted conformations of the TPE groups, which exhibit unhindered intramolecular rotations and experience difficulty in planarising successfully. Consequently the  $\Phi_{\rm S}$  values in hexane are still very low (see Table 3). Similar behaviour has been previously reported for tetraphenylethene in hexane, which exhibits a weak fluorescence emission at approximately 530 nm (PL<sub>max</sub>),<sup>26</sup> compared to 445 nm in the solid state. Excimer formation in these materials is highly unlikely due to the large octyl chains situated at the fluorene 9-position, which weakens the ground state electronic interactions between molecules, which are usually responsible for aggregate formation. Additionally, in our case the fluorescence efficiency is enhanced in the solid state, opposite to excimer formation, which in most cases drastically quenches the fluorescence. Large Stokes shifts

and large differences in the solution and solid state PL emission have been reported for other TPE-based materials.<sup>27</sup>

Although F5-TPE is an oddity (see later), on close inspection of the PL emission peaks for the nanoparticles in 90% water– THF solvent mixture of F(1–4)TPE, it can be observed that they are similar to the solid state. With respect to F(1–3)TPE the PL<sub>max</sub> of the nanoparticles are red-shifted compared to the solid state, which maybe due to the greater aggregation of the molecules in the confined space of the nanoparticles. Red-shifts in the PL of nanoparticles compared to the solid state, for silole and germole materials, have also been previously reported.<sup>28</sup>

The reported F(1-5)TPE materials contain two different chromophores. Therefore, in principle the PL spectra could exhibit two emission profiles. It is well known that the fluorene core exhibits three emissive transitions with defined vibronic structures, representing the (0,0), (0,1) and (0,2) transition peaks, with the (0,0) transition being the highest in energy. The emission profile changes only slightly from solution to the solid state. In contrast tetraphenylethene (TPE) exhibits only one broad peak  $(PL_{max} = 445 \text{ nm})$  with ill-defined vibronic structure. In the solid state F5-TPE exhibits an emission profile with characteristics from both the central fluorene core and the TPE peripheral groups. A comparison of these emission characteristics are shown in Fig. 6. In solution the PL for all F(1-5)TPE materials is barely detectable, however, in the solid state the PL emission profiles for all 5 materials are dominated by TPE. From the solidstate PL spectra of F(1-3)TPE, shown in Fig. 5, it is clear that the emission profiles are not reminiscent of the fluorene core due to the lack of defined vibronic peaks. The emission profiles are broad and featureless with a bathochromic shift, compared to fluorene-only and TPE-only cores, due to the increase in conjugation length. Surprisingly, even when the core of the molecule contains four and five fluorene rings, the broad and featureless emission characteristics of TPE are still present. However, a welldefined vibronic transition around 421 nm is observed, which is characteristic of the (0,0) vibronic peak of the fluorene core. The same peak, albeit weak, is observed for F3-TPE and grows in intensity from F3-TPE to F5-TPE as the fluorene core increases.

 Table 3 Fluorescence quantum yields, nanoparticle dimensions and AIE effect<sup>a</sup>

Fluorophore	$\Phi_{ m S}$				<i>D</i> (nm)	$lpha_{ m F}$	$\alpha_{ m N}$
	Hexane	THF	$arPhi_{ m F}$	$\Phi_{ m N}$			
F1-TPE	0.015	0.003	0.59	0.38	186 (0.124)	196.7	125.3
F2-TPE	0.018	0.008	0.56	0.25	195 (0.165)	70	31.4
F3-TPE	0.019	0.011	0.64	0.31	247 (0.143)	58.2	28.2
F4-TPE	0.018	0.016	0.62	0.39	216 (0.169)	38.8	24.4
F5-TPE	0.024	0.021	0.68	0.41	226 (0.129)	32.4	19.7

<sup>*a*</sup> Abbreviations and definitions:  $\Phi_{\rm S}$  = relative fluorescence quantum yield in solution estimated using 9,10-diphenylanthracene ( $\Phi$  = 0.90 in cyclohexane<sup>29</sup>) as standard,  $\Phi_{\rm F}$  = relative fluorescence quantum yield in PMMA films estimated using 9,10-diphenylanthracene ( $\Phi_{\rm F}$  = 0.83 in PMMA<sup>30</sup>),  $\Phi_{\rm N}$  = relative fluorescence quantum yield for nanoparticles (THF–H<sub>2</sub>O mixture  $f_{\rm w}$  = 90%) estimated using 9,10-diphenylanthracene ( $\Phi_{\rm F}$  = 0.83 in PMMA<sup>30</sup>),  $\Phi_{\rm N}$  = relative fluorescence quantum yield for nanoparticles (THF–H<sub>2</sub>O mixture  $f_{\rm w}$  = 90%) estimated using 9,10-diphenylanthracene ( $\Phi_{\rm F}$  = 0.90 in cyclohexane), D = overall average nanoparticle diameter for THF–H<sub>2</sub>O mixture  $f_{\rm w}$  = 90% at T = 25 °C, (parentheses) = polydispersity index (PDI),  $\alpha_{\rm F}$  = extent of emission enhancement (AIE effect) in the film ( $\Phi_{\rm F}/\Phi_{\rm S}$ ),  $\alpha_{\rm N}$  = extent of emission enhancement (AIE effect) in the nanoparticle ( $\Phi_{\rm N}/\Phi_{\rm S}$ ).



**Fig. 6** Comparison of the solid state PL spectra of oligo-5-fluorene, TPE and F5-TPE.

For F4-TPE and F5-TPE an additional peak at 450 nm and 452 nm, respectively, is observed, which could be the (0,2) transition of the fluorene ring. The greater the fluorene character of the molecule the more defined the emission profile and an increase in the (0,0) transition is observed.

## Aggregation-induced emission (AIE) properties

The AIE behaviour was investigated by monitoring the change in PL intensity with the addition of increasing amounts of water in a THF–water solvent mixture. Here, the THF acts as the solvent and water acts as the antisolvent. Typical AIE behaviour is observed by a transition from isolated molecules to nano-aggregates at a critical concentration of water. This results in a corresponding increase in the PL intensity. Further increasing the water fraction results in a further increase in PL intensity due to further aggregation and the resulting nanoparticles emit light at a higher PL intensity. In most cases the higher the water an initial rise in PL intensity, a drop is observed at approximately  $70\% f_w$  and above.<sup>24a</sup> This has been attributed to molecular agglomeration and the formation of random, amorphous aggregates.<sup>31</sup>

quenching (ACQ) and thus upon aggregation exhibit a reduction in fluorescence intensity compared to its solution state where the molecules are more isolated. For example, a dilute THF solution of oligo-5-fluorene exhibits a reduction in PL intensity after aggregation in 90% water (see Fig. 7). Despite the diminished fluorescence intensity, the long alkyl chains at the fluorene 9-position are very effective in reducing aggregation in the solid state, which minimises the quenching and thwarts significant reduction in the fluorescence intensity. The PL shown in Fig. 8 demonstrates that F(1-5)TPE exhibit the opposite effect and all the end-capped fluorenes show typical AIE behaviour (see Table 3). At water fractions ( $f_w$ ) between 50–90% all the aggregates were homogeneous with no precipitate. At the critical concentration of water the PL intensity starts to increase and continues to increase with higher water contents. The relationship of  $I/I_0$ with water fraction (vol%), see Fig. 8f, shows that the PL intensity is enhanced as the water fraction increases without any reduction in intensity at higher water fractions. Investigation of the ascending PL spectra at low  $f_w$  and from the photos shown in Fig. 9, it can be observed that the critical water concentration for fluorescence "turn-on" is proportional to the molecular weight of the material, with F1-TPE showing the highest critical water concentration of approximately 70%  $f_{\rm w}$ . This is reasonable

Most conventional fluorophores exhibit aggregation caused



Fig. 7 The PL spectra of oligo-5-fluorene ( $R = C_8H_{17}$ ) in THF solution and in a 90% water–THF solution (excitation wavelength = 361 nm, concentration =  $1 \times 10^{-6}$  M).



**Fig. 8** Emission spectra of (a) F1-TPE, (b) F2-TPE, (c) F3-TPE, (d) F4-TPE and (e) F5-TPE in THF–water mixtures with different water contents at concentration =  $1 \times 10^{-6}$  M, excitation wavelength = 361 nm, (f) Changes in PL peak intensities ( $I/I_0$ ) of F(1–5)TPE, in different THF–water mixtures ( $I_0$  = PL intensity in pure THF solution and intensity recorded at 500 nm).

because the molecular weight of F1-TPE is the lowest with the highest solubility in the solvent mixture thus being able to withstand high water concentrations without nucleation. From the photoluminescence quantum efficiency (PLQE) values of the materials in solution and nanoparticle state, we can easily calculate the AIE effect and state the following trends (nanoparticle,  $\alpha_N$ ): F1-TPE (125.3) > F2-TPE (31.4) > F3-TPE (28.2) > F4-TPE (24.4) > F5-TPE (19.7). As the fluorene core is



**Fig. 9** Photos of 1  $\mu$ M F(1–5)TPE in THF–water mixtures with different water fraction increasing from left to right ( $f_w = 0\%$  to 90%), while excited over 365 nm illumination. A = brighter fluorescence with extension of the central fluorene core, B = higher MW F*n*-TPE require less water for fluorescence "turn-on".

elongated the TPE end groups have a weaker influence on the AIE behaviour of the compound. Accordingly, in pure THF solutions F5-TPE is the most efficient emitter (see Fig. 9). Ideally, an efficient AIE material exhibits a large PLQE in the nanoparticle state (or solid state) and a low PLQE in solution. Surprisingly, F5-TPE still exhibits a significant AIE effect even with such a large fluorene core. The AIE effect in the solid state ( $\alpha_F$ ) follows a similar trend. Nanoparticle dimensions were confirmed by DLS and the size, morphology and fluorescent images of the F1-TPE nanoparticles were also confirmed by AFM and fluorescent microscopy (see Fig. 10 and 11). The nanoparticles of all fluorophores are approximately 200 nm in size.



**Fig. 10** AFM shows that the nanoparticles formed from F1-TPE in a mixture of THF–water with 90% water fraction have similar sizes to that obtained from DLS.



**Fig. 11** The fluorescence imaging confirmed AFM results, which indicated F1-TPE forms nanoparticles in a 9 : 1 water:THF mixture.

For F(1-4)TPE at 90%  $f_w$  the PL emission spectra of the nanoparticles are similar to the solid film. However, with respect to F5-TPE the emission spectrum is noticeably different with well-defined vibronic features reminiscent of oligo-fluorenes (see Fig. 8). On closer analysis of Fig. 8e, the PL spectrum at  $80\% f_w$  is similar to its related solid state spectrum and to F4-TPE (Fig. 8d). However, the dramatic change in the emission profile occurs at 85% and 90%  $f_{\rm w}$ . Although not clear from the photos in Fig. 9, in 90%  $f_w$  F5-TPE exhibits bright white fluorescence. Similar to polyfluorene nanoparticles prepared in a similar manner<sup>32</sup> (reprecipitation using solvent and antisolvent system) the F(1-4)TPE nanoparticles reported here are in the amorphous state, like that of the solid state. The PL emission peaks of these nanoparticles are indeed similar to the solid state, although with a trivial slight bathochromic shift. The phase and morphological behaviour that results in changes of the fluorene core conformation has become an essential factor in the photophysics of polyfluorene and to a lesser extent oligofluorene.<sup>19,32</sup> Also, F5-TPE exhibits the lowest  $T_g$  of all the fluorophores. All these aspects may tentatively point to crystallisation as the cause of the unusual PL emission that is shown in Fig. 8e. Interestingly, when the same experiment is performed at a higher F5-TPE concentration (1  $\times$  10<sup>-5</sup> M) in 90%  $f_{\rm w}$  the TPE PL emission is not suppressed and the PL looks similar to that shown for F4-TPE in 90%  $f_{\rm w}$ . Therefore polarity factors due to the increase of the water content are unlikely. Morphology dependent optical properties of AIE-active materials have been reported by other groups.33

The AIE behaviour can be more quantitatively demonstrated by comparing the PLQE values (see Table 3) of the materials in solution ( $\Phi_S$ ), nanoparticles ( $\Phi_N$ ) and solid state ( $\Phi_F$ ). In THF solution the PLQE values increase with elongation of the fluorene core with values calculated at 0.003, 0.008, 0.011, 0.016 and 0.021, for F(1–5)TPE, respectively. In the nanoparticles the PLQE values are enhanced to 0.38 (F1-TPE), 0.25 (F2-TPE), 0.31 (F3-TPE), 0.39 (F4-TPE) and 0.41 (F5-TPE), showing a large increase in the quantum yield. This is a clear demonstration of AIE activity and is opposite to the ACQ effect, in which the addition of water and subsequent aggregation results in lower quantum yields compared to their solution. Some caution must be taken regarding the relative PLQE values of the nanoparticles as they have been shown to be much lower than their absolute values due to the overestimation of the UV absorbance caused by light scattering or the Mie effect.<sup>34</sup> The PLQE in the "solid state" are the highest with F5-TPE reaching 68%. The effectiveness of TPE end-capping at inducing fluorescence quenching can be demonstrated by comparing the PLQE values of the oligo-*n*-fluorenes with and without TPE end-capping. The PLQEs of the oligo-*n*-fluorenes without TPE end-capping, are 0.63<sup>8</sup> (n = 2), 0.75<sup>8</sup> (n = 3), 0.77<sup>8</sup> (n = 4) and 0.96 (n = 5), compared to 0.008 (n = 2), 0.011 (n = 3), 0.016 (n = 4) and 0.021 (n = 5) for F-*n*-TPE.

The AIE phenomenon of TPE-based materials can be best explained by intramolecular effects, and not intermolecular effects, such as  $\pi - \pi$  stacking or J-aggregation. In our case intramolecular effects are more likely because of the amorphous nature of the materials and, secondly, because of the long alkyl chains at the fluorene 9-position. The alkyl chains effectively increase the intermolecular distance, which reduces the van der Waals forces and thus prevents strong intermolecular interactions and close packing of the TPE chromophores. Also, TPE itself is non-planar, in which the dihedral angles of its phenyl rings are around 60°, thus preventing close  $\pi$ - $\pi$  stacking. Another important AIE-active material is 1,1,2,3,4,5-hexaphenylsilole, which exhibits an intermolecular distance of 7.61 Å and is clearly non-planar, which prevents close packing of the molecules.<sup>35</sup> All these factors seem to be in contradiction to a recent publication that suggests the AIE phenomenon to be due to intermolecular effects.<sup>36</sup> The PL emission is enhanced in the solid state because of the restricted rotational and vibrational motions of the phenyl rings around the TPE double bond, thus blocking non-radiative pathways. In solution fast non-radiative relaxation is dominant because the vibrational and rotational motions of the phenyl rings are significant. Accordingly, the PLQEs are enhanced in the solid state compared to the solution.

The importance of intramolecular effects in explaining the enhanced fluorescence emission can be found in examining the optical properties of dilute dispersions (Abs = <0.1) of F(1-5) TPE materials in a rigid polymethylmethacrylate (PMMA) matrix. These blend films were prepared by spin casting approximately 0.4 to 1% by weight ratios of F(1-5)TPE materials in PMMA (0.1 g ml<sup>-1</sup> DCM). It is worth mentioning that in much larger weight ratios (10 to 16%) using oligofluorenes Clark and co-workers regarded the oligo-n-fluorene molecules in PMMA blends as isolated and non-interacting.<sup>37</sup> We were able to repeat the PLQE of oligo-5-fluorene (1 wt%) in PMMA (96%, using diphenylanthracene as the standard), with good agreement to the literature value (95%, absolute value). The PLQE of oligo-5-fluorene in THF was calculated at 96% and identical to the PMMA matrix, which also suggests the molecules to be isolated in PMMA at this concentration. Therefore, with similar weight ratios of F(1-5)TPE in PMMA, compared to oligo-5-fluorene, we can also regard the molecules as isolated. Isolated molecules in dilute solutions of THF are unhindered and free to rotate. However, in a rigid PMMA matrix internal rotations are restricted due to the dramatic reduction in the free volume and subsequently the PLQE of F1-TPE reaches 0.59. This is dramatically higher compared to the solution state (0.003) and is reminiscent of a molecular rotor, therefore, suggesting intramolecular processes being responsible for the enhanced luminescence. Furthermore, for the case of F1-TPE in a PMMA matrix, the PL spectrum shows an identical emission profile

compared to its pristine thin film, however, with a slight blueshift. Similar experiments using other AIE-active materials have been carried out by other research groups that involve frozen dilute solutions in dioxane in which the PL intensity is observed to increase when the temperature is decreased to -20 °C.<sup>28</sup> Also, solvents with high viscosity such as paraffin oil have been used to confirm that the AIE phenomenon is due to intramolecular effects.<sup>38</sup>

In an attempt to further understand the nature and importance of the internal rotations of the TPE moiety and its influence on the optical properties of our end-capped oligomers, we designed and synthesised F1-PP. Reducing the internal rotations of tetraphenylethane by locking two phenyl rings together, as shown in Scheme 3, should prevent fluorescence quenching and enhance photoluminescence properties in solution. Compound 10 can be oxidised to the corresponding phenyl phenanthrene derivative using DDO as the oxidant.<sup>39</sup> From GC-MS analysis no starting material was observed and, surprisingly, 10% of the chloro derivative was detected, presumably picking up the chlorine atom from the DDQ molecule. However, this impurity is not detrimental to the Suzuki coupling and was not removed. Using quinine sulfate as the standard ( $\Phi = 0.54$  in 0.1 M H<sub>2</sub>SO<sub>4</sub><sup>40</sup>) the PLQE of F1-PP was calculated at 53%, which is much higher than the PLQE of F1-TPE. In addition F1-PP does not exhibit AIE properties. Of course high PLOE in solution of rigid molecules is not a new insight, nonetheless in this respect the comparison with F1-TPE is relevant because it demonstrates the importance of internal rotations of the TPE groups and its effect on fluorescence quenching. Therefore, we can safely confirm that the internal rotations of the TPE terminal groups play an important role in determining the materials fluorescence efficiencies. In comparison with F1-TPE, F1-PP exhibits blueshifts in its absorption and emission maxima (see Fig. 12), which



Scheme 3 (a) DDQ, DCM (dry),  $CH_3SO_3H$ , 0 °C to RT, (b) *n*-BuLi (2.5 M), THF (dry), -78 °C, (ii) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, (c)  $K_3PO_4$ , Pd(PPh<sub>3</sub>)<sub>4</sub>, DMF (dry), 90 °C.



**Fig. 12** UV-VIS absorption of F1-PP in THF, PL spectra of F1-PP in THF solution (excitation = 345 nm) and in powder form (excitation = 361 nm).

interestingly implies less overlap of the  $\pi$ -electrons and a reduction in the conjugation length.

### Real-time fluorescence imaging and solid-state vapour sensing

The fact that F(1-5)TPE exhibits AIE properties with bright cyan emission enabled real-time monitoring of the morphology evolution during solvent evaporation. Fig. 13 reveals that nucleation sites formed first in the earlier stage, followed by ripple-like growth. The individual ripple-like growth further enlarged and became elongated as time lapsed, and eventually emerged into the morphology of "sardine bait balls" rounded up by dolphins. This structure, which resembles massive sardines swarming in a tight ball, suddenly disappeared and was replaced with large spherical-like structures. Some cores of the spheres still contained solvent and thus appeared dark in the fluorescence imaging while others were free of solvent, thus emitting a bright cyan colour. Finally, all the spheres were dried into discs and at this moment, some much smaller spheres appeared. A portion of the smaller spheres again was not completely free of solvent and thus they had dark cores. This is probably the very first example to reveal morphology changes as molecules assemble into nanostructures and microstructures using fluorescence imaging.



Fig. 13 Real-time fluorescence imaging of F1-TPE during solvent evaporation, solvent = DCM, concentration =  $10^{-12}$  M.

When dried patterns made of F1-TPE were exposed to organic solvent vapour, the PL intensity of such patterns would become dimmer. Such intriguing properties of Fn-TPEs have the potential to be used as solid-state chemical sensors for volatile organic vapours (Fig. 14).

### **Electrochemical properties**

The electrochemical behaviours of these compounds were determined by cyclic voltammetry using a standard three-electrode electrochemical cell in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) dissolved in distilled dichloromethane. The working electrode was glassy carbon, the counter electrode was a platinum wire, and the reference electrode was Ag/Ag<sup>+</sup> (0.1 M). Thus, the HOMO levels were calculated to be -5.86, -5.87, -5.84eV, -5.82 and -5.83 eV by the method  $-(E_{ox} + 4.70)$  reported by Li *et al.*<sup>41</sup> (Table 4). These HOMO levels are very similar to those of oligofluorene.42 The HOMO levels of these compounds are even close to that of the most widely used NPB (5.4 eV), suggesting the hole-injection barriers from NPB to the compounds are minimum. Their LUMOs were obtained from optical band gap energies (estimated from the onset wavelength of their UV absorptions) and HOMO values, which gave LUMO values in the range of -2.78to -2.84 eV, which is close to the electron affinity of tri(phenyl-2benzimidazolyl)benzene (TPBi) (2.7 eV).

#### **Electroluminescence** properties

Electroluminescence of F(1–5)TPE was investigated due to their high solid-state photoluminescence, amorphous behaviour and high thermal stabilities. We fabricated multilayer OLED devices with configuration ITO/PEDOT (40 nm)/Fn-TPE ( $\sim$ 50 nm)/ TPBi (40nm)/LiF (1 nm)/Al (100 nm) by spin coating deposition processes, in which Fn-TPE materials serves as the emitting layer, PEDOT functions as the hole-transporting layer and TPBi functions both as the hole-blocking and electron transporting layer. As shown in Fig. 15, after being fabricated into LED devices, the EL spectra of F3-TPE have emission characteristics



**Fig. 14** Patterns formed from F1-TPE were deposited on glass substrates (left: control; right: sample). The control was never exposed to organic vapour, but the sample was exposed to dichloromethane with exposure time listed on the left. After 20 s exposure, the photoluminescence of F1-TPE was completely turned off, demonstrating its ability to detect organic vapours.

Table 4EL properties<sup>a</sup>

Fn-TPE	$\lambda_{\rm EL}$ (nm)	$V_{\rm on}\left({\rm V} ight)$	$L_{ m max}$ (cd m <sup>-2</sup> )	$\eta_{ m P,max} \ ( m lm \ W^{-1})$	$\eta_{\mathrm{C,max}} \ (\mathrm{cd}\ \mathrm{A}^{-1})$	HOMO (eV)	LUMO (eV)	$E_{\rm g}({\rm eV})$
F1-TPE	468	5.8	1300	1.0	2.6	-5.858	-2.779	3.079
F2-TPE	468	5.5	1100	0.55	1.5	-5.868	-2.836	3.032
F3-TPE	488	6.4	1050	0.5	1.6	-5.842	-2.829	3.013
F4-TPE	476	6.2	1050	0.6	1.8	-5.816	-2.813	3.003
F5-TPE	480	4.8	120	0.06	0.2	-5.826	-2.830	2.996

"Abbreviations:  $\lambda_{EL} = EL \max$ ,  $V_{on} = turn on voltage$ ,  $L_{max} = maximum brightness$ ,  $\eta_{P,max} = maximum power efficiency$ ,  $\eta_{C,max} = maximum current efficiency$ , HOMO = ionisation potential, LUMO = electron affinity,  $E_g = optical band gap$ .

similar to the PL spectra. The devices based on F(1-5)TPE exhibits a maximum luminance  $(L_{max})$  of 1300, 1100, 1050, 1050 and 120 cd m<sup>-2</sup>, a maximum current efficiency ( $\eta_{c,max}$ ) of 2.6, 1.5, 1.6, 1.8 and 0.2 cd A<sup>-1</sup> and a maximum power efficiency ( $\eta_{P,max}$ ) of 1.0, 0.55, 0.5, 0.6 and 0.06 lm  $W^{-1}$ , respectively. The detailed EL performances are listed in Table 4. The materials LUMO levels seem to be well matched with the electron affinity of TPBi. However, the large barriers for hole injection at the anode due to the high ionisation potentials of the fluorophores result in rather high turn-on voltages (higher than 4.8 V). The barriers for charge injection seem to be the lowest for F5-TPE due to the comparatively lower turn on voltage for its OLED device. However, in contrast the current efficiency is the lowest with  $\eta_{c,max} = 0.2$  cd  $A^{-1}$ . The  $L_{max}$  appears to follow a trend of decreasing brightness as the fluorene core is extended from one fluorene unit to five fluorene units, with F1-TPE exhibiting the highest brightness.

From the EL data, it can be concluded that F1-TPE is the best OLED emitter and the turn-on voltages and efficiencies can be tuned by the length of the fluorene core.

## Conclusions

We have synthesised a series of amorphous fluorene-based materials end-capped with TPE groups that exhibit superior thermal properties compared to their analogous fluorene-only materials that are not end-capped with TPE. Interestingly, TPE end-capping activates "aggregation induced emission" and the materials quench in solution, contrary to the nanoparticles and solid state that exhibit strong fluorescence. Comparative studies of their AIE effect reveal that as the fluorene core is elongated the TPE end groups have a weaker influence on the AIE behavior of the compound. Therefore, F1-TPE is the most efficient AIE



Fig. 15 (A) EL spectra of F3-TPE, (B) change in luminance and current density with the applied bias, (C) luminance versus power efficiency, (D) luminescence versus current efficiency.

fluorophore compared to F(2-5)TPE. From THF-water solvent mixture experiments we observe a gradual increase of the PL intensity with increasing water concentrations, reaching a maximum at 90% v/v water content with high PLQE. At this water concentration the particles are of nano-size dimensions with an overall average diameter of approximately 200 nm. Additionally, the highest solid state PLQE was observed for F5-TPE, which reached a value of 68%. We have shown that F1-TPE can be used as a solid state solvent vapour sensor with very visible "on-off" fluorescence behaviour. Encouraged by their high PLQEs and amorphous behaviour OLEDs were fabricated and from the EL data F1-TPE exhibits the best OLED properties, with a turn on voltage of 5.8 V,  $L_{\text{max}} = 1300 \text{ cd m}^{-2}$ ,  $\eta_{\text{P,max}} =$ 1 lm W<sup>-1</sup> and  $\eta_{C,max} = 2.6$  cd A<sup>-1</sup>. These TPE end-capped oligofluorenes represent an interesting class of linear, amorphous AIE-active materials that exhibit intriguing optical properties.

# Experimental

#### General procedure for the Pd-catalysed Suzuki cross-coupling

Dibromo-*n*-fluorene (2, 7 or 8, limiting reactant), boronic acid/ ester (11 or 16, 2.1–2.4 eq.), tetrabutylammonium hydrogen sulfate (10 mol%) and  $K_2CO_3$  (5 eq.) were added to a toluene:H<sub>2</sub>O (2 : 1 v/v ratio) mixture and the system was evacuated, with the aid of a vacuum pump, and filled with nitrogen 3 times. Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%) was added and again the reaction vessel was evacuated and purged with nitrogen. The reaction was heated at 90 °C for 24 h. Water (20 ml) and toluene (10 ml) were added and the toluene layer separated and subsequently removed using a rotary evaporator. The crude product was purified by gravity column chromatography (silica gel) eluting with DCM–hexane solvent mixture to yield a yellow-green solid.

## F1-TPE

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 0.65 (quint, 4H), 0.79 (t, 6H), 1.03–1.18 (m, 20H), 1.96–2.00 (m, 4H), 7.06–7.14 (m, 34H), 7.43 (d, 4H, *J* = 8.4 Hz), 7.52 (m, 4H), 7.70 (d, 2H, *J* = 8.0 Hz). MS *m/z* (APCI): 1051.9 (M<sup>+</sup>).

Elemental analysis, expected (%): C 92.52, H 7.48, obtained

# F2-TPE

(%): C 92.27, H 7.33.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.77–0.81 (m, 20H), 1.07– 1.19 (m, 40H), 2.01–2.05 (m, 8H), 7.04–7.16 (m, 34H), 7.45 (d, 4H, J = 8.4 Hz), 7.54 (overlapping d, 2H), 7.56 (d, 2H, J = 1.2 Hz), 7.61 (overlapping d, 2H), 7.64 (dd, 2H, J = 1.2 Hz, 7.6 Hz), 7.73 (m, 4H).

MS m/z (APCI): 1440.9 (M<sup>+</sup>).

Elemental analysis expected (%): C 91.74, H 8.26, obtained (%): C 91.67, H 8.24.

# F3-TPE

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.77–0.80 (m, 30H), 1.07–1.19 (m, 60H), 2.03–2.11 (m, 12H), 7.05–7.14 (m, 34H), 7.44 (d, 4H, J = 8.4 Hz), 7.54 (overlapping d, 2H), 7.56 (overlapping d,

2H), 7.61–7.66 (m, 8H), 7.73 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 7.6 Hz), 7.80 (d, 2H, *J* = 7.6 Hz).

MS *m*/*z* (APCI): 1828.6 (M<sup>+</sup>).

Elemental analysis, expected (%): C 91.29, H 8.71, obtained (%): C 91.11, H 8.75.

# F4-TPE

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.73–0.87 (m, 40H), 1.08– 1.25 (m, 80H), 2.04–2.13 (m, 16H), 7.05–7.18 (m, 34H), 7.46 (d, 4H, J = 8.4 Hz), 7.55–7.70 (m, 16H), 7.75–7.82 (m, 8H).

MS *m*/*z* (MALDI-TOF): 2217.1 (M<sup>+</sup>).

Elemental analysis, expected (%): C 91.00, H 9.00, obtained (%): C 90.91, H 8.96.

## F5-TPE

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.76–0.85 (m, 50H), 1.09– 1.26 (m, 100H), 2.05–2.12 (m, 20H), 7.06–7.17 (m, 34H), 7.46 (d, 4H, J = 8.0 Hz), 7.56–7.71 (m, 20 H), 7.75–7.85 (m, 10H).

MS *m*/*z* (MALDI-TOF):2605.3 (M<sup>+</sup>).

Elemental analysis, expected (%): C 90.79, H 9.21, obtained (%): C 90.59, H 9.09.

## F1-PP

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.61–0.74 (m, 4H), 0.80 (t, 6H), 1.08–1.22 (m, 20H), 2.06–2.10 (m, 4H), 7.20–7.38 (m, 14H), 7.46–

7.75 (m, 20H), 7.80 (d, 2H, *J* = 8.0 Hz), 8.85 (d, 4H, *J* = 8.3 Hz). MS *m*/*z* (APCI): 1047.9 (M<sup>+</sup>).

Elemental analysis, expected (%): C 92.88, H 7.12, obtained (%): C 92.55, H 6.98.

HPLC = 96.4% (2 : 8, DCM:hexane, CN column).

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