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Near-Infrared Fluorescent Nanoparticles Formed by Self-Assembly of Lipidic (Bodipy) Dyes

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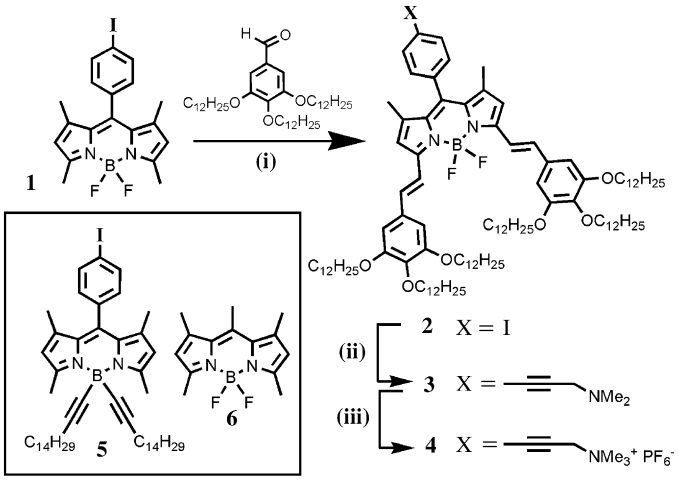
Fluorescent organic nanoparticles (FONs) formed from π-conjugated frameworks are of immense interest in materials science,[1] most notably as advanced means for imaging of intact biological systems and delivery vehicles.[2] In particular, fluorescent nanoparticles engineered from polymer-doped dyes[3] or small molecules[4] allow fine-tuning of the emissive properties, at least over a restricted wavelength range in the visible window. The highpoint of this research is the intercalation of multiple dyes of disparate optical properties into one-dimensional heterostructures[5] or to promote fluorescence resonance energy transfer within the FONs as a means to induce white-light emission.[6] Small molecular dopants, desirable for cost effectiveness, present special problems in this field since they are prone to segregation into microstructures or aggregates that serve as dark quenchers of local fluorescence.[7] However, in certain cases, emissive aggregates can be assembled from rather small molecules, such as hexaphenylsilole, that themselves are nonemissive when dispersed as monomers.[8] The extension of this work has led to the formulation of systems with which organic dyes are translocated into FONs by light-driven self-assemblies that provide a means of fluorescence enhancement.[9]

Boron-dipyrromethene (Bodipy) dyes, being uncommonly popular fluorescent labels, are susceptible to aggregation in polar solvents and in the solid state. The resultant supramolecular assemblies can be used to tune the color of OLEDs[10] or to examine structure–function relationships for proteins and lipid membranes.[11] In general, the apolar Bodipy dyes form H- or J-aggregates due to facile stacking of the electron-rich dipyrromethene core. In the former structures, the Bodipy planes stack in parallel to give essentially nonfluorescent species featuring a blue-shifted absorption profile.[12] In the J-aggregate, the transition dipoles are not parallel but oriented in planes mutually tilted by an angle governed by the presence of appendages along the Bodipy core. Such aggregates, or dimers, are weakly fluorescent and usually exhibit a modest red-shifted absorption spectrum, which can be well interpreted by conventional excitonic coupling theory.[13] In specific cases, formation of H- and J-aggregates can be controlled by host–guest complexation,[14] macrocyclization,[15] multilayering in polyelectrolytes,[16] and by confinement in sol-gel matrices,[17] or liquid crystalline phases.[18,19]

In seeking to manipulate the type of self-aggregation undertaken by functionalized Bodipy dyes, attention has turned to a central platform decorated with an ammonium cation at the tip and multiple paraffin chains at the outer periphery (Scheme 1). The intention was to achieve a balance between stacking induced by the hydrophobic chains and electrostatic repulsion caused by the localized cationic residues. In particular, it was anticipated that attenuation of the latter charges might be realized by adoption of a tilted geometry that restricted the number of monomers accreted into the final structure. To attain this goal, preliminary materials were designed around trialkoxyphenyl fragments and trimethylammonium head-groups.



Scheme 1. Outline of the synthesis protocols used to prepare key intermediates leading to the isolation of the pivotal blue dye **4**. (i) Toluene, piperidine, *p*TsOH (tr), 140 °C, 53 %; (ii) dimethylaminopropyne, [Pd(PPh$_3$)$_2$Cl$_2$] (6 mol %), CuI (10 mol %), benzene, TEA, 50 °C, 82 %; (iii) CH_3I, THF, room temperature, 3 h, 75 %, followed by anion exchange with KPF_6 in a mixture of THF/water. The insert gives the structures for the yellow dyes **5** and **6** needed for intercalation studies and as reference compounds.

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The target molecule **4** was prepared in three steps from **1** through a double Knoevenagel reaction carried out on 3,4,5-tridodecyloxybenzaldehyde under basic conditions leading to **2** in good yield.[20] The 16.2 Hz proton–proton coupling constant for the double bond at 7.27 ppm in the ^{1}H NMR spectrum confirmed the *trans* conformation of the vinylic bond. Subsequent cross-coupling with dimethylaminopropyne provided **3** in fair yield. Alkylation of the tertiary amine appears facile by using iodomethane and affords the stable cationic species **4**. The observation of a singlet at 2.64 ppm in the ^{1}H NMR spectrum, at the expense of the singlet at 2.24 ppm for the tertiary amine **3**, is diagnostic of the course of the reaction. Metathesis of the counter anion is performed at will.

The absorption and emission spectra of **4** are typical of a blue distyryl-based Bodipy dye with a $S_0 \rightarrow S_1$ transition centered at 646 nm, a second absorption transition peaking at 370 nm and a fluorescence maximum at 669 nm. A fluorescence quantum yield (Φ_F) of 40% and an excited-state lifetime (τ_S) of 4.1 ns are in keeping with a singlet emitter. Interestingly, progressive addition of water (from 0 to 65%, v/v) to a tetrahydrofuran (THF) solution of **4** resulted in shifting of the absorption maximum to 737 nm (Figure 1a). The final solution remained transparent and homogeneous over several weeks without apparent change of the absorption and emission properties (Figure 1a, inset). The shape and the bathochromic shift are clear signatures of J-aggregation[21] and are in agreement with similar features reported for cyanine dyes.[22] Above 65% water precipitation of the dye occurred. On irradiation at 380 nm, a sharp emission was observed at 743 nm, for which Φ_F was 6% and τ_S was reduced to 0.27 ns (Figure 1b). The changes in fluorescence could be observed by the naked eye (Figure 1b, inset). The excitation spectrum followed the absorption spectrum, and thereby confirmed that the J-aggregate is responsible for the fluorescence found at 743 nm. We could not exclude that the shift in absorption and emission wavelength could be due to a combination of conformational effects and charge transfer contributions as currently scrutinized in oligoacene molecular crystals.[23]

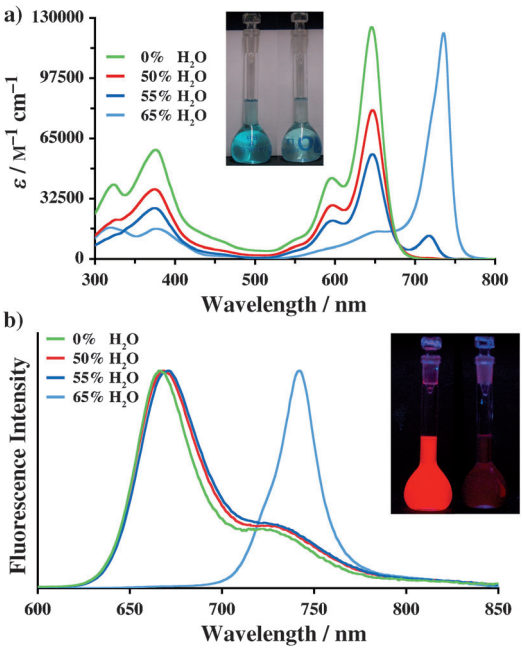

Figure 1. Spectroscopic changes observed during addition of water to a THF solution of **4**, the concentration of the dye in the final mixture was 5×10^{-6} M. a) Evolution of the absorption spectrum as the water content increased from 0 to 65% (v/v); the insert shows photographs of the original THF solution (left) and after addition of 65% (v/v) water (right) under ambient light. b) Evolution of the fluorescence spectrum (λ_{exc} = 380 nm) under the same conditions; the insert shows photographs of the fluorescence stimulated by UV illumination.

Dynamic light scattering (DLS) carried out on a solution of **4** in THF containing water (65% v/v water) revealed the presence of spherical nanoparticles with a narrow size distribution of 1.4 to 1.6 nm. These objects are designated as **4-agg**. During aging of the mother liquor for 4 weeks no noticeable changes in the nanoparticle size were observed (Figure 2a). Larger particles (>10 nm) were observed upon using greater quantities of water. The particle size and distribution was confirmed by transmission electron microscopic (TEM) studies (Figure 2b and c) and reproduced with several fresh solution of **4-agg** ($\sim10^{-6}$ M).

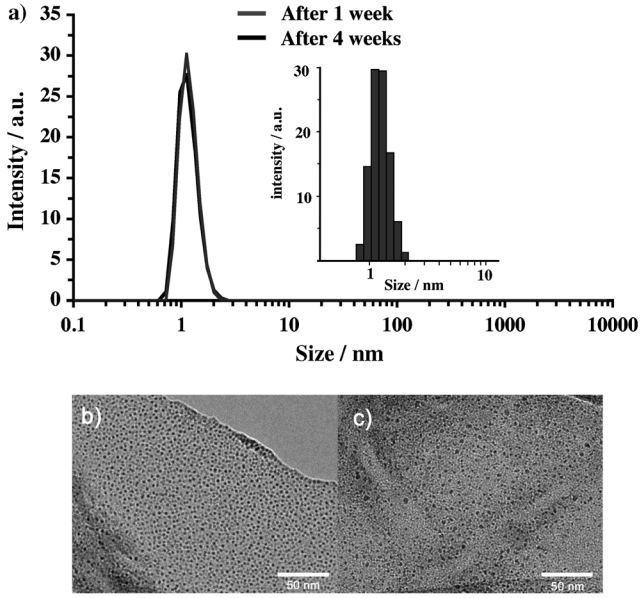

Figure 2. a) Dynamic light scattering analysis of a THF/water (65% v/v) solution of **4-agg** (5×10^{-6} M) and after aging the solution. b) TEM image of the same solution drop-cast and evaporated to dryness, overnight, on a copper grid with a carbon membrane; c) sample prepared from a fresh solution of **4-agg** (3.6×10^{-6} M); scale bars: 50 nm.

The next challenge was to examine the ability of the nanoparticle to sequester dye molecules from solution in such a way as to form functional units. A convenient test system involves decorating the nanoparticles with a yellow Bodipy dye that absorbs predominantly at 500 nm, at which

the blue dye is almost transparent. To this end, the nanoparticles were prepared in the presence of dye **5**, a less-conjugated Bodipy dye bearing paraffinic chains but lacking the cationic residue, which absorbs at 500 nm and emits strongly at 520 nm ($\Phi_F = 90\%$, $\tau_S = 5.3$ ns). The addition of dye **5** (20 mol%) to the **4-agg** nanoparticles did not perturb the absorption or emission profiles but slightly altered the emission wavelength (from 743 to 733 nm). Furthermore, the particle size distribution as determined by DLS was similar to that of untreated **4-agg** (Figure S3 in the Supporting Information). The excitation spectra recorded in the presence of **5** (20 mol%) shows that photons absorbed by the yellow dye are efficiently transferred to **4-agg** (Figure 3a). We can conclude from these observations that **5** (guest) is intercalated into the nanoparticle where it acts as the donor for electronic energy transfer to the blue aggregate **4-agg** (host). Furthermore, estimation of band intensities at 500 nm and at 737 nm indicates that the energy transfer efficiency from the guest to the host is close to 100%. Model calculations[24] by using Förster theory indicate that the critical distance for through-space energy transfer in this system is about 29 Å, and thereby precludes the possibility that the yellow dye lies outside the nanoparticle. It is likely that the small amount of residual yellow emission ($\Phi_F = 1.2\%$) arises from **5** not assimilated into the nanoparticle (Figure 3a).

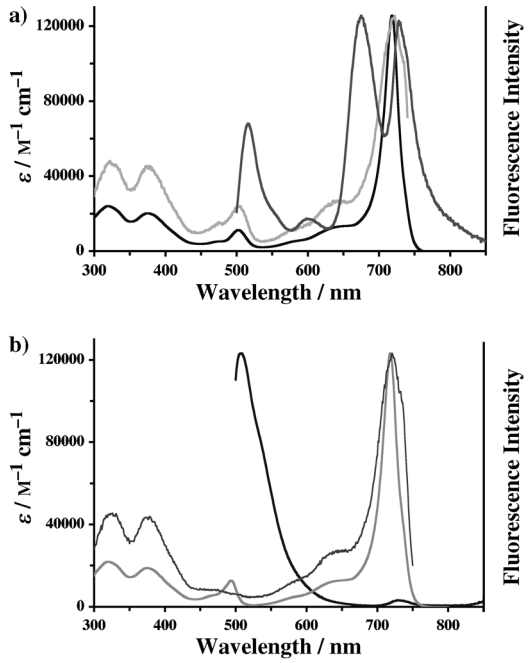

Figure 3. Spectroscopic changes accompanying the doping of the blue nanoparticles (5.5×10^{-6} M) in THF/water (65% v/v) with a yellow dye (**5** or **6**). a) Absorption spectra of **4-agg** (5.5×10^{-6} M) in THF/water (65%) containing dye **5** (20 mol%; ——) and emission spectra obtained by excitation at 490 nm (——). Excitation spectra were plotted by scaling the emission at 760 nm (——). b) Absorption of the same solution of **4-agg** but after addition of **6** (20 mol%; ——) and emission spectra by excitation at 490 nm (——). Excitation spectra was plotted by scaling the emission at 760 nm (——).

Support for this hypothesis was provided by replacing the hydrophobic dye **5** with a related derivative **6** lacking the paraffinic chains. Thus, when **6** (20 mol%) was added to the **4-agg** nanoparticles under identical conditions to those employed above, energy transfer did not take place. Instead, **6** emitted strongly ($\Phi_F = 67\%$; $\tau_s = 5.1$ ns) at 520 nm, and emission from the aggregate at 743 nm was extremely weak. This latter weak fluorescence arises from direct excitation of the blue aggregate **4-agg** at 490 nm as confirmed from inspection of the excitation spectrum ($\lambda_{em} = 760$ nm), which shows no contribution from the yellow dye in the region around 500 nm (Figure 3b). It is concluded on the basis of the energy transfer results that paraffin chains are essential to promote uptake of the dye into the nanostructure.

Returning now to the system comprising **5** intercalated into the nanoparticles, it was shown that a new fluorescence band appears with a maximum at 667 nm as the loading of **5** approaches 20 mol% (Figure 3a). This latter emission band could be explained either: 1) by formation of a dimeric form of **5** embedded in the blue nanoparticles, by analogy with lipid domains in cell membranes,[25] that does not contribute to the energy transfer process to the nanoparticles as indeed expressed by the excitation spectra (Figure 3a); or 2) the insertion of dye **5** in the nanoparticle likely modifies the aggregation of **4** in the nanoparticle and restores the emission that can be observed when the water content is lower, generating a signal at 670 nm. The emission quantum yield of the nanoparticle ($\Phi_F = 4.8\%$) remains comparable to that measured in the absence of **5**; this means that the dimer does not trap excitation energy from the aggregated blue dye. More significantly, it was concluded from close examination of the corresponding excitation spectra that photons absorbed by the dimer were not transferred to the aggregated blue Bodipy that forms the nanoparticles (Figure 3b).

In fact, the excitation spectrum recorded for emission from the nanoparticle contains a small contribution from monomeric **5**, indicating that this species exists in equilibrium with the dimer. The excitation spectrum recorded for the dimer is dominated by the absorption at 520 nm. It is important to note that the size distribution of the nanoparticle remains insensitive to the degree of loading of **5**, even when the latter is extensively aggregated (Figure S1 in the Supporting Information). Addition of water to a solution of pure **5** in THF (5×10^{-6} M) induced flocculation of the dye within a couple of minutes. The supernatant exhibited several emission bands, most notably at 605 and 667 nm, that can be assigned to dimeric species by comparison with other simple Bodipy dyes (Figure S6 in the Supporting Information). Note that the emission of the dimer in solution for **5** at 667 nm is the same as that of the dimer incorporated in the blue aggregate, **4-agg**. The nanoparticle protects **5** against large-scale flocculation but permits formation of the emissive dimer at a site that is unfavorable for excitation energy transfer to the nanoparticle. Presumably, the dimer is located in lipid-like regions provided by the paraffinic chains whereas the monomer is mobile and approaches more closely to the Bodipy head-groups. The fact that the

presence of **4-agg** prevents precipitation of dye **5** is good indication that **5** is sequestered inside the self-assembled nanostructure.

A final goal relates to the concepts of reversibility of the accretion process and recovery of the entrapped yellow dye. This objective was successfully achieved simply by raising the concentration of THF from 35 to 50% in an aqueous dispersion of **4-agg** containing 20 mol% of **5** (Figure 4a). This treatment regenerates the absorption spectrum characteristic of **4** ($\lambda_{abs}=646$ nm) contaminated with **5** ($\lambda_{abs}=500$ nm; Figure 4a). Under these conditions, DLS measurements confirmed the absence of nanoparticles and larger objects. In parallel, steady-state emission spectra displayed the expected red fluorescence at 670 nm of the blue dye **4** together with strong emission at 520 nm due to the yellow dye **5** ($\Phi_F=90\%$). This reversibility could be easily followed with the naked eye, with the apparition of the bright-red emission at around 650 nm (Figure S3 in the Supporting Information). By careful manipulation of the composition of the water/THF mixture, it was possible to recycle many times between nanoparticles and monomeric species without obvious fatigue or degradation of the dyes. Finally, control studies showed that electronic energy transfer from **5** to **4** is negligible in solution at micromolar concentrations.

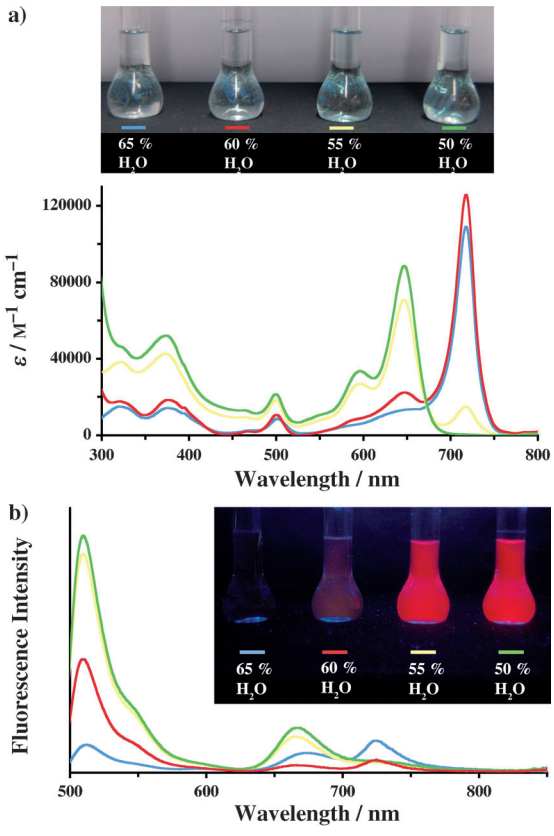

Figure 4. Spectroscopic changes observed on varying the solvent composition of **4-agg** (2.7×10^{-6} M) THF/water solution containing dye **5** (5.3×10^{-7} M). a) Absorption spectra recorded for water (65%; ——), 60% (——), 55% (——), and 50% (——). b) Fluorescence spectra recorded under excitation at 490 nm of the same four solutions. The concentrations of dyes were kept constant for all solutions.

In summary, we have reported on the self-assembly of a new type of discrete nanoparticle emitting in the NIR and formed from a fluorescent organic dye. The self-assembly process is quantitative and the resultant nanoparticle has a very narrow size distribution consistent with the accretion of a small number (four to five) of dye molecules in which the paraffin chains are shrunk at the center of the FONs and the polar head-groups are at the periphery of the object and solvated by water molecules. A snapshot of the resulting aggregates is illustrated in Figure 5.

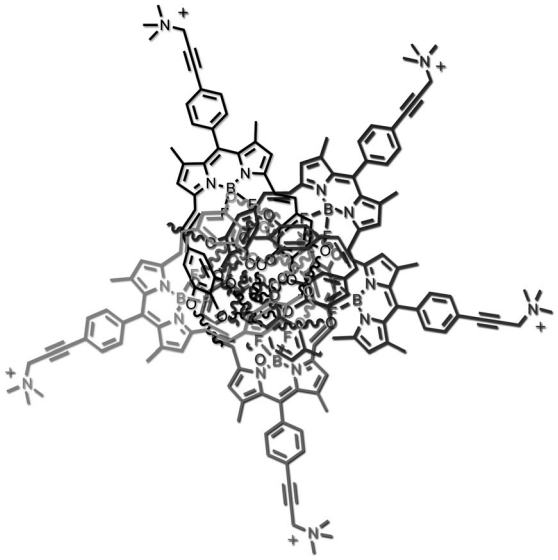

Figure 5. Schematic representation of five molecules (arbitrary number) of dye **4** self-assembled in a THF/water solution.

Controlled aggregation of this type is driven by the cooperative balance of an electrostatic repulsion at the periphery and lipophilic associations at the core, and leads to the appearance of emission in the near-IR. These particles are unexpectedly stable over many weeks standing, without precipitation. The actual composition of the system is determined by the amount of water added to a THF solution of the monomeric blue dye and can be cycled many times by changing the mole fraction of water. The nanoparticles act as a sponge (host) for added dye molecules (guest), provided that the latter are equipped with complementary lipophilic chains. In this way, advanced photon collectors that emit at 760 nm can be assembled and subsequently dismantled at will. These interactive nanoparticles are likely to possess important applications as delivery vehicles for living cells in which internalization of the particle can be monitored by fluorescence microscopy. Dispersion of the nanoparticles in flexible films has already been demonstrated and will be used to address a single particle.

Experimental Section

Compound 2: Compound **1** (200 mg, 0.44 mmol, 1 equiv), 3,4,5-tridodecylalkoxybenzaldehyde (1.2 g, 1.82 mmol, 4 equiv) and PTSA (5 mg, 0.03 mmol) were dissolved in toluene (25 mL) and piperidine (1 mL) in a round-bottom flask equipped with a Dean Stark apparatus. The resulting solution was heated at 140 °C until all the solvents were collected by the Dean Stark apparatus. Toluene (25 mL) and piperidine (1 mL) were added to the solid reaction media and the dryness protocol was repeated four times. Purification by chromatography on silica gel (50:50 to 100:0 dichloromethane/petroleum ether) followed by precipitation (CH_2Cl_2/EtOH), afforded **2** as a dark-blue solid (400 mg, 0.23 mmol, 53 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.88$ (d, $^3J = 15.9$ Hz, 2H), 7.51 (d, $^3J = 8.1$ Hz, 2H), 7.11 (d, $^3J = 15.9$ Hz, 2H), 6.75 (s, 4H), 6.56 (d, $^3J = 15.9$ Hz, 2H), 6.38 (s, 2H), 4.05 (t, $^3J = 6.3$ Hz, 4H), 3.78 (t, $^3J = 6.30$ Hz, 8H), 1.81–1.25 (m, 96H), 0.87 ppm (t, $J = 6.3$ Hz, 18H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 153.8$, 153.4, 141.2, 140.5, 138.2, 137.5, 136.9, 135.2, 133.3, 132.1, 130.9, 118.7, 118.3, 106.8, 94.2, 73.4, 69.1, 32.3, 30.2, 30.1, 30.0, 29.8, 26.7, 23.1, 14.4 ppm; UV/Vis (THF): λ nm (ε, $M^{-1}cm^{-1}$): 319 (31400), 377 (49200), 598 (50500), 648 (121500); EI-MS m/z (nature of the peak): 1731.19 ([M], 100); calcd for $C_{105}H_{170}BF_2IN_2O_6$: C 72.80, H 9.89, N 1.62; found: C 73.06, H 9.79, N 1.42.

Compound 3: [$Pd(PPh_3)_2Cl_2$] (2.5 mg, 0.004 mmol) and CuI (1.1 mg, 0.006 mmol) were added to an argon-degassed solution of **2** (100 mg, 0.06 mmol) and 1-dimethylamino-2-propyne (20 μL, 0.18 mmol) in benzene/triethylamine (10/2 mL), and the reaction mixture was heated at 60 °C for 48 h. The solution was then poured into H_2O (10 mL) and extract with CH_2Cl_2 (3×15 mL). The organic phase was washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. Purification by chromatography on silica gel (99:1 to 99:5 dichloromethane/methanol) afforded **3** as a dark-blue solid (83 mg, 82 %). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 8.37$ (d, $^3J = 16.2$ Hz, 2H), 7.39 (d, $^3J = 8.1$ Hz, 2H), 7.30 (d, $^3J = 16.2$ Hz, 2H), 6.97 (s, 4H), 6.63 (d, $^3J = 8.3$ Hz, 2H), 6.38 (s, 2H), 4.29 (t, $^3J = 5.7$ Hz, 4H), 3.81 (t, $^3J = 6.3$ Hz, 8H), 3.34 (s, 2H), 2.24 (s, 6H), 2.02–1.92 (m, 4H), 1.78–1.64 (m, 12H), 1.53–1.33 (m, 80H), 0.93 ppm (t, $J = 6.3$ Hz, 18H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 154.1$, 153.5, 141.7, 140.8, 138.2, 137.7, 135.3, 133.7, 132.4, 132.3, 124.5, 119.1, 118.5, 107.1, 87.1, 85.0, 73.6, 69.2, 48.7, 44.2, 32.35, 31.09, 30.31, 30.30, 30.25, 30.21, 30.17, 30.01, 29.85, 29.68, 29.66, 26.76, 26.68, 23.11, 14.35 ppm; UV/Vis (THF): λ nm (ε, $M^{-1}cm^{-1}$): 329 (30353), 381 (49777), 602 (39107), 648 (119500); EI-MS m/z (nature of the peak): 1686.25 ([M], 100); calcd for $C_{110}H_{178}BF_2N_3O_6$: C 78.30, H 10.63, N 2.49, O 5.69; found: C 78.62, H 10.30, N 2.20.

Compound 4: Iodomethane (10 μL, 0.15 mmol) was added to a solution of **3** (70 mg, 0.04 mmol) in distilled THF (5 mL). The solution was stirred at 20 °C for 3 h and then poured into 20 mL of an aqueous solution of KPF_6 (2 mmol, 368 mg). The organic phase was extracted with CH_2Cl_2 (3×20 mL) and washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. Purification by chromatography on silica gel (99:3 to 99:15 dichloromethane/methanol) afforded **4** as a dark-blue sticky solid (55 mg, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.66$ (d, $^3J = 8.3$ Hz, 2H), 7.53 (d, $^3J = 16.2$ Hz, 2H), 7.40 (d, $^3J = 7.8$ Hz, 2H), 7.17 (d, $^3J = 15.9$ Hz, 2H), 6.78 (s, 4H), 6.62 (d, $^3J = 8.3$ Hz, 2H), 6.38 (s, 2H), 4.43 (s, 2H), 4.05–3.97 (m, 12H), 3.35 (s, 9H), 2.10–1.99 (m, 12H), 1.82–1.51 (m, 108H), 0.93 ppm (t, $J = 6.3$ Hz, 18H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 153.32$, 152.87, 141.70, 139.85, 139.12, 137.52, 134.92, 133.11, 132.30, 131.73, 131.63, 128.62, 124.03, 117.99, 106.42, 86.30, 84.58, 73.59, 69.27, 53.175, 48.62, 44.38, 31.92, 31.89, 31.85, 30.35, 29.75, 29.72, 29.69, 29.63, 29.54, 29.48, 29.44, 29.37, 29.31, 26.20, 26.13, 26.10, 22.63, 14.91, 14.08 ppm; UV/Vis (THF): λ nm (ε, $M^{-1}cm^{-1}$): 334 (34322), 382 (54200), 604 (49612), 651 (125690); EI-MS m/z (nature of the peak): 1702.33 ([M]$^+$, 100); calcd for $C_{111}H_{181}BF_8N_3O_6P$: C 72.17, H 9.88, N 2.27; found: C 72.40, H 10.12, N 2.04.

Preparation of 4-agg and doped nanoparticles: H_2O (6.5 mL) was added dropwise over a 5 min period to a solution of **4** in 3.5 mL of THF (5×10^{-6} M). The resulting solution was left at ambient temperature, overnight, and then analyzed by spectroscopy, DLS and TEM. For the doped nanoparticles the same procedure was used but with the addition of 5 to 20 mol % of dyes **5** or **6**.

Reversibility tests: The mother solution of the nanoparticles was diluted with THF by using volumetric flasks in order to maintain the concentration of dye **4** constant at around 2.7×10^{-6} M. The resulting solution was left at ambient temperature, overnight, and then analyzed by spectroscopy and DLS.

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Keywords: energy transfer · fluorescent nanoparticles · host–guest interactions · microscopy · self-assembly

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