



## Facile pathways to multichromophoric arrays based on a truxene platform

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### ABSTRACT

Multi-branched dyes were synthesized using a truxene platform appropriately functionalized with iodo residues, the key step here being a controlled iodination process giving access to mono-, di-, tri- and hexa-derivatives. Conversion of the iodo compounds to the corresponding alkynes followed by cross-coupling with iodophenylindacenes catalysed by Pd(0) or with chloro-Pt(II) complexes catalysed by Cu(I) enabled the introduction of multiple chromophore/luminophore units. Both neutral and cationic species involving Pt(II) centres were obtained in excellent yields. Connection of ethynylpyrene units to boron within the hexa-grafted truxene Bodipys provided very efficient cascade singlet energy transfer from the pyrene to the yellow emitter. Irradiation in the truxene core also resulted in quantitative energy transfer to the organic dyes.

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In recent years, the engineering of artificial systems devoted to collection and concentration of photons has attracted significant attention.<sup>1,2</sup> As a rule, such systems contain a molecular platform consisting of luminescent modules (transition metal complexes, organic dyes or luminescent polymers) connected via unsaturated bridges. The concept is to absorb light at several equivalent sites and transport all photons to a single, different emitting or reacting site. Provided energy transfer is rapid relative to deactivation, the result is concentration of the incident light energy.

The same principle applies to photosynthetic organisms that use light-harvesting centres to optimize absorption of solar energy, and then transfer this excitonic energy to the reaction centre, where it is used to bring about reactions such as oxidation of water and reduction of carbon dioxide.<sup>3</sup> Nature has ideally organized the chromophores, and relays in such a way that each step of the collection process is very fast (subpicosecond regime). Chemists have learnt how to carefully design artificial systems mimicking some of these fundamental processes, and many have found application in energy conversion devices,<sup>4</sup> redox switches, photonic wires and gates,<sup>5</sup> and logic systems.<sup>6</sup>

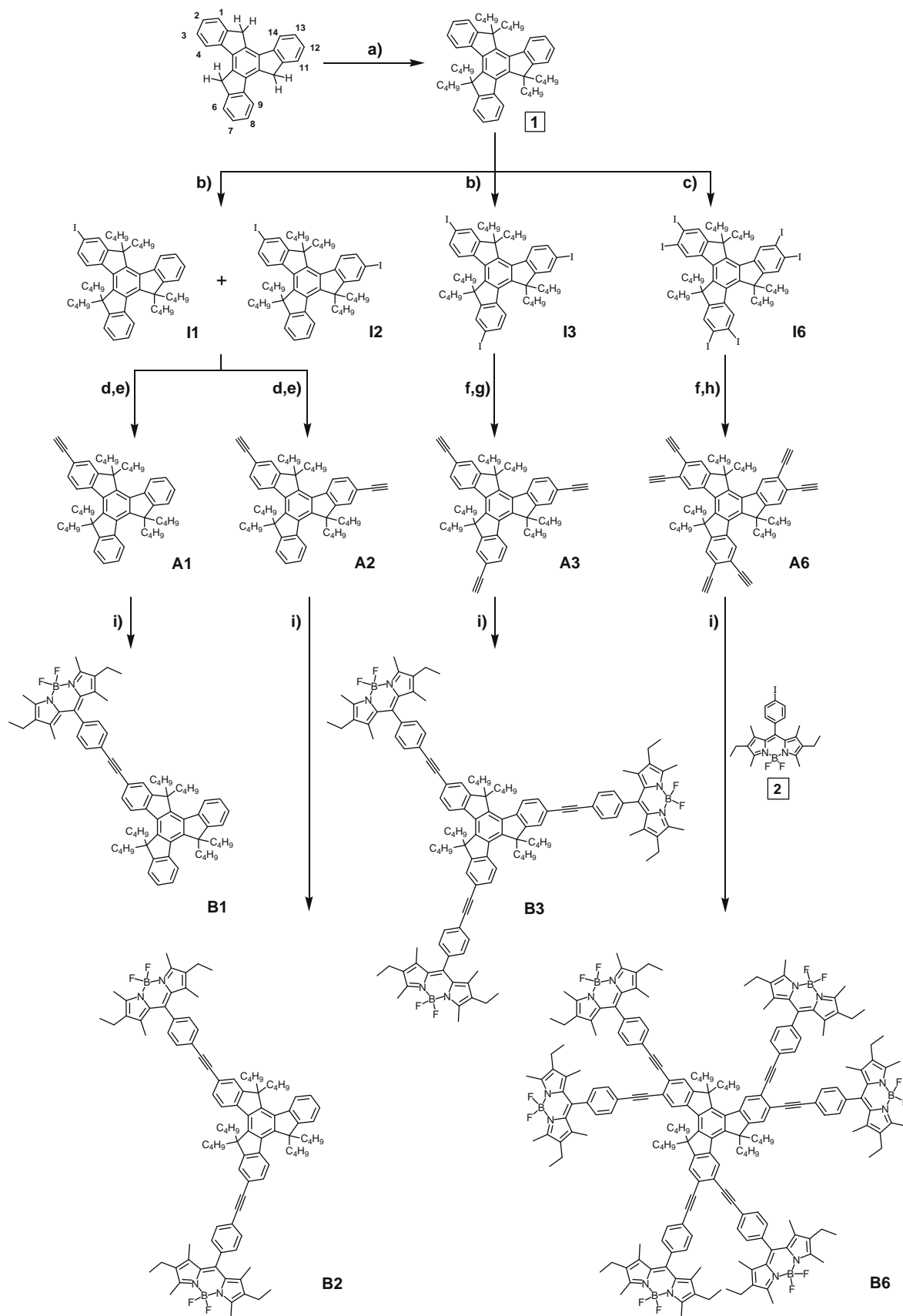
Truxene (10,15-dihydro-5H-diindeno[1,2-a;1',2'-c]-fluorene) is a planar heptacyclic aromatic system,<sup>7</sup> which can be formally regarded as a C<sub>3</sub>-symmetrically fused fluorene trimer. During the past decades, it had been recognized as potential starting material for the construction of liquid crystalline compounds,<sup>8</sup> bowl-shaped fragments of fullerenes<sup>9</sup> and C<sub>3</sub>-tripodal materials for chiral recognition.<sup>10</sup> Recently synthesized derivatives include a variety of star-shaped oligomers and dendritic truxene derivatives with extended  $\pi$ -conjugation<sup>11</sup> of the polyaromatic core, as well as truxene-based

donor–acceptor systems for use as multifunctional fluorescent probes.<sup>12</sup>

In this contribution we report the synthesis, characterization and some optical properties of a series of novel truxene derivatives bearing one to six chromophoric units appended to the central truxene core via ethynyl linkers. Highly fluorescent difluoro-bora-diaza-s-indacene (*F*-Bodipy) derivatives or polyimine Pt(II) fragments were connected as branches to the truxene moiety via metal-catalyzed cross-coupling reactions.

The target ethynyltruxene derivatives **A1–A6** were synthesized starting from the readily available hexabutylated truxene **1**, which was obtained by peralkylation of the anions of the truxene lithium salts.<sup>13</sup> Although the selective mono- and di-iodination of truxene derivatives have been described in the literature,<sup>14</sup> in our case the reactions always provided a mixture of mono- and di-iodinated compounds which could not be purified by column chromatography, and necessitated tedious and repetitive recrystallizations. Thus, the mixture of mono and di-iodinated compounds **I1** and **I2** was directly reacted with propargyl alcohol via palladium-catalyzed cross-coupling reaction. The polarity brought by the alcohol functions allowed direct separation of the mono- and bis-propargylic substituted derivatives by column chromatography. The corresponding ethynyl derivatives **A1** and **A2** were obtained by treatment with manganese oxide and potassium hydroxide. Triiodinated truxene **I3** was obtained by treatment with a mixture of iodine and iodic acid, while increasing the reaction temperature as well as the iodine/iodic acid amount led to the formation of the hexasubstituted compound **I6**. Reaction of **I3** and **I6** with (trimethylsilyl)acetylene using Pd(0) catalysis and subsequent treatment with either potassium fluoride or potassium carbonate afforded the corresponding ethynyl derivatives **A3** and **A6** in good yields (see Scheme 1).

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**Table 1**  
Selected data for compounds **A1–A6**, **B1–B6** and **P12**

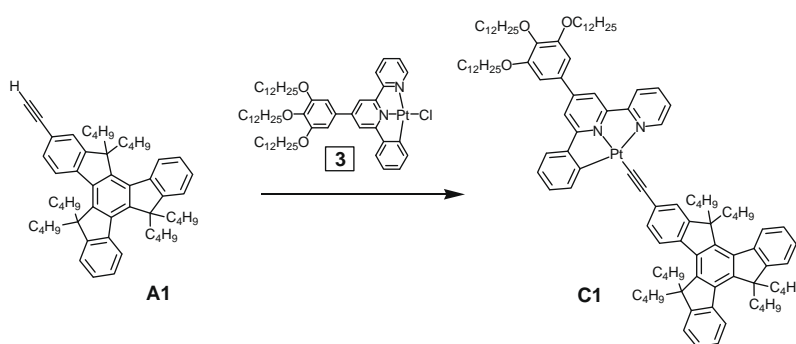
Compound	Yield (%)	MS <sup>a</sup>	$\lambda$ (nm), $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) <sup>b</sup>	$\lambda_{em}$ (nm) <sup>b</sup>	$\phi_{em}$ <sup>c</sup>	$\tau$ (ns)	$k_r$ <sup>d</sup> (10 <sup>8</sup> s <sup>-1</sup> )	$k_{nr}$ <sup>d</sup> (10 <sup>8</sup> s <sup>-1</sup> )
<b>A1</b>	66	702.4	325 (40900)	361, 378	0.20	17.5	0.11	0.457
<b>A2</b>	70	727.0	325 (92300)	365, 383	0.21	18.2	0.12	0.434
<b>A3</b>	92	750.3	326 (159700)	369, 387	0.23	20.3	0.11	0.379
<b>A6</b>	93	822.4	334 (95800)	370, 389	0.22	18.3	0.12	0.426
<b>B1</b>	74	1080.5	527 (77900) 333 (59900)	540	0.80	5.0	1.60	0.40
<b>B2</b>	79	1484.0	527 (149300) 337 (117700)	540	0.75	5.4	1.39	0.46
<b>B3</b>	78	1887.1	526 (189000) 339 (152900)	540	0.57	5.3	1.08	0.81
<b>B6</b>	84	3094.0	526 (407000) 351 (182200)	542	0.72	5.2	1.38	0.54
<b>P12</b>	72	5567.6	523 (438000) 371 (799000)	538	0.80	5.5	1.45	0.36

<sup>a</sup> Electron impact mass spectrometry, referring to [M]<sup>+</sup>, for **P12** MALDI-TOF in dichloromethane solution.

<sup>b</sup> Determined in aerated dichloromethane solution, ca.  $5 \times 10^{-6}$  M.

<sup>c</sup> Quantum yield of emission, calculated using quinine bisulfate ( $\phi_{em} = 0.55$  in H<sub>2</sub>SO<sub>4</sub> 1 N,  $\lambda_{exc} = 366$  nm) as reference for compounds **A1–A6** and rhodamine 6G ( $\phi_{em} = 0.78$  in water,  $\lambda_{exc} = 500$  nm),<sup>15</sup> as reference for compounds **B1–B6** and **P12**, all  $\phi_{em}$  are corrected for changes in refractive index.

<sup>d</sup> Radiative and non-radiative rate constants  $k_r$  and  $k_{nr}$  calculated using the following equations:  $k_r = \phi_F/\tau_F$ ,  $k_{nr} = (1 - \phi_F)/\tau_F$ .



**Scheme 2.** Reagents and conditions: CuI, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N, rt, 72 h, 82%, anaerobic conditions.

After some experimentation, we succeeded in preparing compounds **B1**, **B2**, **B3** and **B6** bearing one, two, three and six Bodipy fragments, respectively, by reacting stoichiometric amounts of the ethynyl-truxene derivatives with the iodophenyl-Bodipy derivative **2**<sup>16</sup> under classical Pd(0) cross-coupling conditions. No decrease in yields was observed in increasing the number of Bodipy linkages (see Table 1).

In an effort to incorporate other chromophores and in analogy with the previous reactions, we decided to functionalize the truxene core with luminescent oligopyridine d<sub>8</sub>-Pt(II) complexes (Scheme 2).

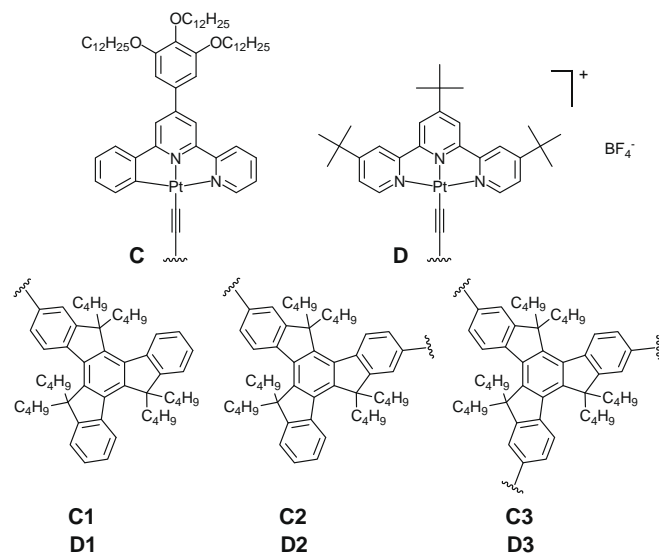
To avoid possible solubility problems associated with unsubstituted (phenylpolypyridine)Pt(II) units, we used orthometallated (6-phenyl-2,2'-bipyridine)Pt(II) precursors bearing the tridodecyl-oxypyphenyl moiety.<sup>17</sup> The connection to the truxene core was promoted by CuI leading to the neutral complex **C1** in 82% yield. Analogous (*tert*-butyl-terpyridyl)Pt(II) truxene derivatives were obtained from (4,4',4''-*tert*-butyl-2,2':6',2''-terpyridine)Pt(II) chloride under similar conditions.<sup>18</sup> Neutral or cationic mono-, di- and tri-nuclear complexes were obtained in good yields (Chart 1).

The functionalization opportunities offered by the Bodipy family of compounds enabled us to extend the light-harvesting abilities of the hexasubstituted compound **B6**. Displacement of the fluorine atoms in favour of the formation of a boron-ethynyl bond can be achieved by using a Grignard reagent. Thus, 1-ethynylpyrene was reacted with ethylmagnesium bromide to form the corresponding Grignard derivative, and then allowed to react with compound **B6**. Complete boron functionalization occurred in good yield (72%), and afforded **P12** bearing 12 pyrene fragments on its periphery (see Scheme 3).

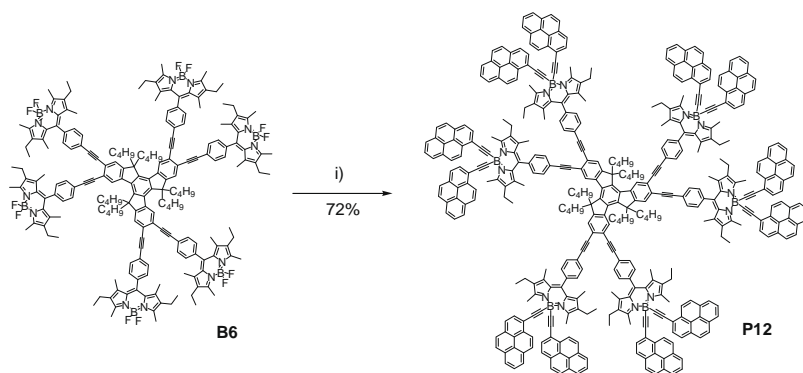
All compounds were unambiguously characterized by <sup>1</sup>H and <sup>13</sup>C NMR, electron impact mass spectrometry and elemental anal-

ysis. In particular, the well-resolved NMR spectra for all compounds excluded the presence of aggregates.

<sup>1</sup>H NMR spectra for compounds **B1**, **B6** and **P12** are shown in Figure 1. For **B1**, the characteristic signals corresponding to the truxene alkyl chains as well as to the substituents on the Bodipy core can be clearly identified in the aliphatic region. The aromatic signals are quite complex due to the lack of symmetry in **B1**, but an AB signal (7.53 ppm,  $J_{AB} = 8.2$  Hz,  $\nu_{AB} = 123.0$  Hz) can be safely



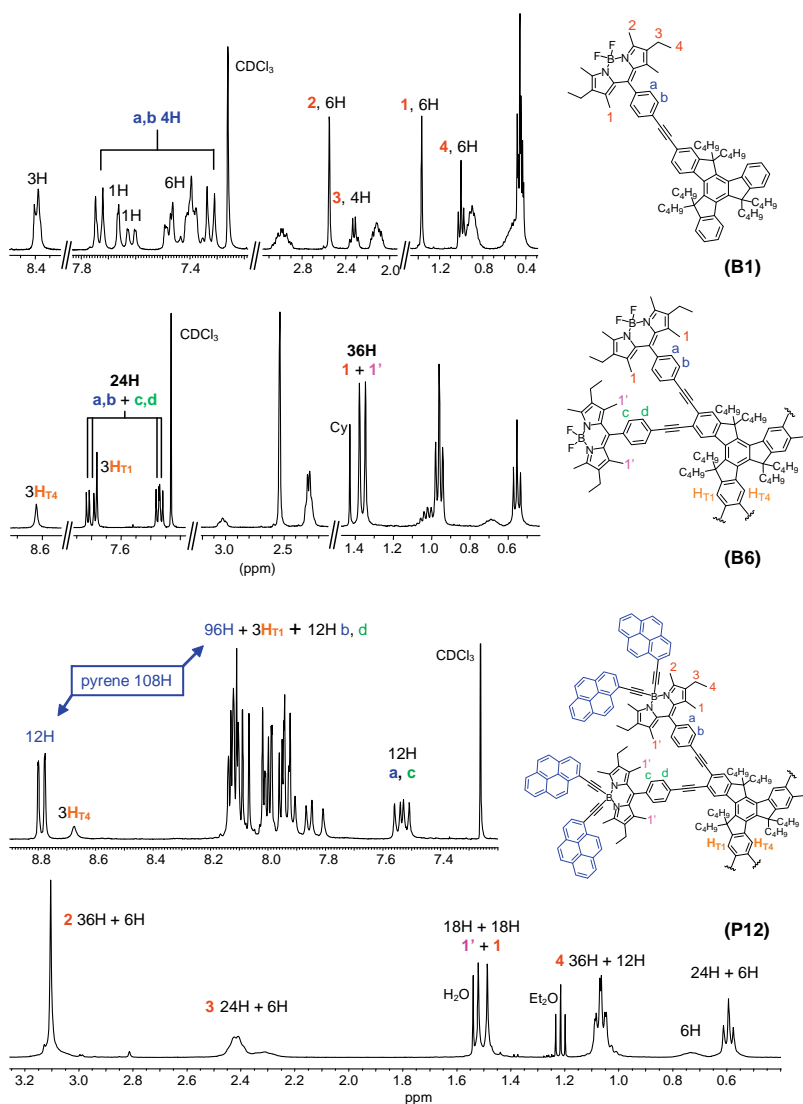
**Chart 1.**



**Scheme 3.** Reagents and conditions: 1-ethynylpyrene, EtMgBr, THF, 60 °C, 18 h.

attributed to the protons on the phenyl ring in the *meso* position of the Bodipy. When six bodipy fragments are connected to the truxene core (**B6**), the aromatic pattern becomes much simpler, with two singlets corresponding to the six protons remaining on the truxene moiety and two distinct AB signals referring to the protons

*ab* and *cd* of the *meso* phenyl groups. In the aliphatic region, two singlets at 1.38 and 1.35 ppm accounting for protons 1 and 1' confirm that the Bodipy fragments at the C 2,7,12 positions differ chemically from those at the C 3,8,13 positions. For **P12**, the presence of the 12 pyrene fragments is consistent with a characteristic



**Figure 1.** Proton NMR (400.1 MHz) spectra measured in CDCl<sub>3</sub> at room temperature for key dyes **B1** (top), **B6** (middle) and **P12** (bottom).

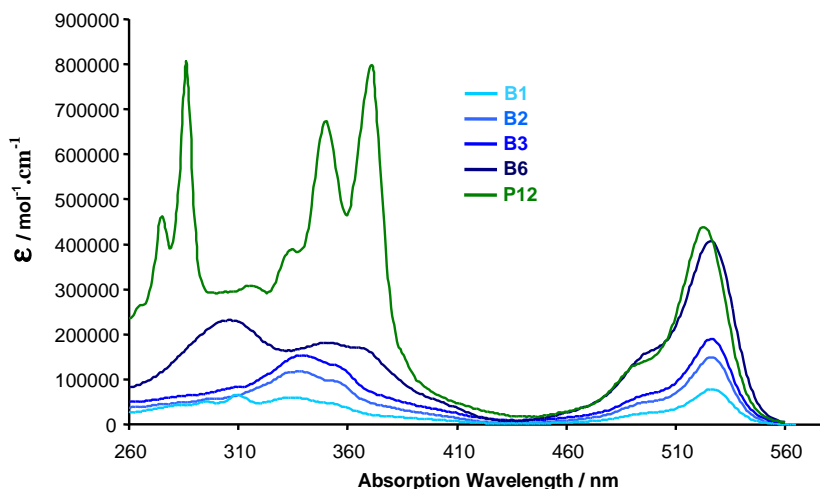


Figure 2. Absorption spectra recorded for the different truxene-Bodipy dyes in  $\text{CH}_2\text{Cl}_2$  solution at rt.

doublet at 8.78 ppm ( $^3J = 9.2$  Hz). The aliphatic part is comparable to that in **B6** although the alkyl signals of the truxene chains are less well resolved due to the aromatic pyrene envelope.

As shown in Figure 2, compounds **B1** to **B6** present essentially the same absorption profile. The intense absorption band at 526 nm which is approximately proportional to the number of fluorophore branches can be attributed to the  $S_0 \rightarrow S_1$  transition located on the Bodipy core. The spectral region between 310 and 410 nm shows absorption bands, which progressively increase in intensity from **B1** to **B6** and are assigned to  $\pi-\pi^*$  excitations of the truxene units and  $S_0 \rightarrow S_2$  of the Bodipy cores. Note that for **P12**, the additional strong absorptions located near 270 and 370 nm and displaying well-resolved fine structure are due to transitions belonging to the pyrene subunits.

The emission spectra for compounds **B1** to **B6** are shown in Figure 3. All compounds show a single emission at 540 nm, which is characteristic of Bodipy emission and independent of the excitation wavelength. Excitation in the truxene absorption range of 310–340 nm produced no truxene emission at 362 nm. In a similar way, excitation in the pyrene transitions does not provide any residual pyrene emission but only that from Bodipy. Clearly, quantitative intramolecular energy transfer from the truxene core or pyrene fragments is effective in these multichromophoric systems.

As would be expected from this, the excitation spectra match the absorption spectra over the complete absorption range, which is a clear indication of energy transfer and that all modules participate in the energy-transfer process. Spectroscopic data for all dyes are gathered in Table 1.

All the platinum complexes exhibit a strong absorption, around 477 nm for **C1–C3** and in the range 496–512 nm for **D1–D3**, corresponding to a metal-to-ligand charge-transfer transition (MLCT) with a contribution of ligand (alkyne-truxene)-to-ligand (terpy or phenylbipy)-charge transfer (LLCT). The former series phosphoresce at 622 nm and the latter at 649 nm, values in keeping with previous studies on mono-nuclear complexes.<sup>19</sup>

Our design opens up the possibility of engineering sophisticated dyes bearing photon absorbers at the periphery and at the core, and energy transducers in the inner layer. All photons would be funnelled to a low-energy acceptor (Bodipy) before the final emission. Direct grafting of platinum modules via  $\sigma$ -alkyne tethers provides phosphorescent multi-nuclear complexes in which the inherent fluorescence of the truxene is quenched by the MLCT and LLCT states of the complex. Work in progress is focused on increasing the dimensionality of these multi-branched systems and on introducing additional energy relays in order to promote multi-FRET energy devices. Such a strategy

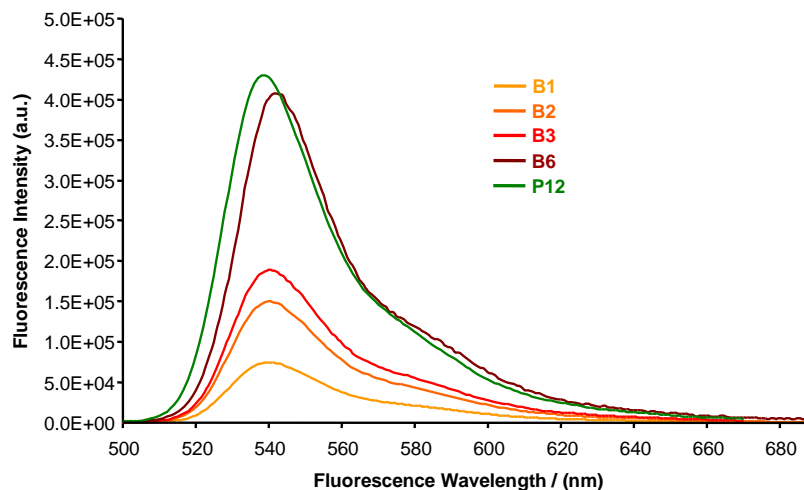


Figure 3. Emission spectra recorded for the different Bodipy dyes linked to truxene in  $\text{CH}_2\text{Cl}_2$  solution at rt. Excitation wavelength = 330 nm.

requires distinction of the different reacting sites on the truxene platform. Further work is in progress to obtain multi-cascade molecular devices.

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