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# Highly efficient energy transfer in BODIPY–pyrene decorated cyclotriphosphazene

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# 1. Introduction

Supramolecular systems containing two or more chromophores have attracted the interest of the scientific community due to their potential for important applications ranging from light harvesting and storage to sensors and optoelectronic devices [1,2]. Such considerations have led to the preparation and characterization of a large number of dendritic constructs decorated with different chromophores selected for their specific photophysical properties. The study of the photophysical properties of these compounds is particularly interesting and highly dependent on the functional dye systems [3,4] Although many photoactive dendritic constructs have been documentated to date, only a few articles about 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene cores (borondipyrromethene, BODIPY)-pyrene systems have been published [5]. Pyrenes are also part of a very important family of fluorophores, which have been widely studied in macromolecular and materials science. The unique photophysical properties of pyrene and its ability to form an excimer led to a widespread use as a fluorescent label in various macromolecules [6-8]. Several photoactive units have been incorporated into pyrenes in order to tune their electronic and photophysical properties [9,10]. The BODIPY dyes are especially

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# ABSTRACT

In this study, two different cyclophosphazene compounds bearing five pyrene units and one borondipyrromethene unit were designed and synthesized. All compounds were fully characterized by elemental analysis, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. The photophysical properties of the new compounds were investigated by means of absorption and fluorescence spectroscopies in dilute dichloromethane solutions. Both systems exhibit a highly efficient energy transfer process, from the excited pyrene units to the borondipyrromethene units. The photophysical studies indicated that the compounds exhibit large Stokes' shifts unlike reference simple BODIPY dyes.

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suitable for this purpose due to their bright high absorption coefficients, high fluorescence yields, long excited state lifetimes, and good solubility in organic solvents [11]. However, most BODIPY dyes have the fatal disadvantage because of their small Stokes' shift. A small Stokes' shift can cause self-quenching and errors in the measurement of excitation light and scattered light. Both of these can decrease the detection using advanced fluorescence techniques. Therefore, BODIPY dyes with larger Stokes shifts would be potentially useful for fluorescence bioassays [12,13].

The phosphazenes are an important class of inorganic heterocyclic ring systems in fundamental and applied science [14]. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides or amines on halocyclophosphazenes or higher polymers [15] and their physical and chemical properties can be tailored via appropriate substituted groups on phosphorus atoms. Additionally phosphazenes are relatively inert and stable to a variety of reaction conditions. There has been recently considerable interest in fluorescent compounds based on cyclic phosphazene cores [16,17] or cyclolinear polymers with the cyclotriphosphazene units [18,19] for development of electroluminescent devices.

Hexachlorocyclotriphosphazene might be an excellent scaffold to anchor two or more chromophores. To our best knowledge, there is no report of synthesis of pyrene and BODIPY being linked to cyclotriphosphazene together. Therefore, to combine BODIPY and pyrene chromophores we desired the use of cyclotriphosphazene as a platform. In this work, we describe the







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Fig. 1. Structure of pyrene–BODIPY substituted (3 and 4) cyclic phosphazenes.



Fig. 2. The reference compounds 5 and 6.

synthesis and characterization of compounds **3** and **4** (Fig. 1). Compounds **3** and **4** were studied by absorption and emission spectroscopy to investigate from pyrene to BODIPY energy transfer. Cyclophosphazene compounds exhibit excellent optical performance with a high energy transfer efficiency (up to 99%) and large Stokes' shift (up to 75 nm).

# 2. Experimental

# 2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from *n*-hexane. CDCl<sub>3</sub> was employed for NMR spectroscopy and the following chemicals were obtained from Merck; BF<sub>3</sub>.OEt<sub>2</sub>, 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ), magnesiumperchlorate [Mg(ClO<sub>4</sub>)<sub>2</sub>], 2,4dimethyl pyrrole, 4-hydroxybenzaldehyde, 1-hydroxypyrene, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, TFA, triethylamine, silica gel 60, tetrahydrofuran, dichloromethane, 1,8,9-Anthracenetriol for MALDI matrix were obtained from Fluka. 4-Dimethylaminobenzaldehyde was obtained from Alfa-Aesar. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

#### 3. Equipment

Absorption spectra in the UV–visible region were recorded with a Shimadzu 2101 UV Pc spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using 1 cm path length cuvettes at room temperature. Mass spectra were acquired in linear modes with average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. 1,8,9-Anthracenetriol MALDI matrix yielded the best MALDI-MS spectra. 1,8,9-anthracenetriol (20 mg/mL in tetrahydrofuran) matrix for compounds **3** and **4** were prepared. MALDI samples were prepared by mixing compounds **3** and **4** (2 mg/mL in tetrahydrofuran) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf micro tube. Finally 1  $\mu$ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. <sup>13</sup>P, <sup>1</sup>H



Scheme 1. Chemical structure and synthetic pathway of 1-4.

and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solutions and on a Varian 500 MHz spectrometer.

# 4. The parameters for fluorescence quantum yields

The fluorescence quantum yield value of the sample (**3** and **4**) was determined in dichloromethane by comparing with the fluorescence of Rhodamine 6G as a standard. Fluorescence quantum yields ( $\Phi_F$ ) were calculated by the comparative method (Eq. (1)) [20],

$$\Phi_{\rm F} = \Phi_{\rm F} \left( {\rm Std} \right) \frac{F \cdot A_{\rm Std} \cdot n^2}{F_{\rm Std} \cdot A \cdot n_{\rm Std}^2} \tag{1}$$

where  $\Phi_{\rm F}({\rm Std})$  is the fluorescence quantum yield of standard. Rhodamine 6G was employed as the standard ( $\Phi_{\rm F} = 0.76$  in water) [21]. *F* and *F*<sub>Std</sub> are the areas under the fluorescence emission curves of sample (**3** and **4**) and the standard, respectively. *A* and *A*<sub>Std</sub> are the respective absorbance of the samples and standard at the excitation wavelengths. The concentration of the solutions at the excitation wavelength fixed at  $5 \times 10^{-7}$  mol dm<sup>-3</sup>. According to the Eq. (2) [22,23], where  $\Phi$ ENT is the energy transfer quantum yield,  $\Phi_{\rm F}$  (dyad) and  $\Phi_{\rm F}$  (donor) are the fluorescence quantum yields of the dyad (the donor part) and the donor without connecting to the acceptor, respectively.

$$\Phi_{\rm ENT} = 1 - \Phi_{\rm F(dyad)} / \Phi_{\rm F(donor)}$$
(2)

# 4.1. Synthesis

The reference compounds **5** [24] and **6** [25] were prepared and purified according to the literature procedure (Fig. 2).

# 4.2. Synthesis of 1,1,3,3,5-pentachloro-5-(4-formylphenoxy) cyclotriphosphazatriene (**1**)

4-hydroxybenzaldehyde (0.35 g, 2.88 mmol) and finely powdered dry potassium carbonate (0.4 g, 2.88 mmol) were dissolved in dry THF (10 mL) under argon atmosphere. The solution was transferred into a 50 mL dropping funnel and slowly dropped to the solution of trimer, N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> (1.0 g, 2.88 mmol) in dry THF (10 mL) under argon atmosphere in a 50 mL three-necked roundbottomed flask. The reaction mixture was stirred for 2 days under an atmosphere of argon and the reaction followed by TLC. The formed potassium chloride (KCl) was removed by filtration, the solvent removed under reduced pressure, and the resulting white powder was subjected to column chromatography using dichloromethane-hexane (1:1) as eluant. Compound **1** is highly viscous oil; Yield: 0.45 g (36%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 6.6-6.7$  (m, 4H, ArCH),  $\delta = 9.12$  (s, 1H, -CHO). {<sup>1</sup>H}<sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 22.51$  [d, 2P,  $>\underline{P}(Cl)_2, A_2], 11.72 [t, 1P > \underline{P}(OPhOCHO)(Cl), X], ^2J_{P,P} = 62.46 \text{ Hz}, MS$ (MALDI-TOF) m/z (%):433 (100) [M + H]<sup>+</sup>. Elemental analysis: (found: C 18.95, H 1.08, N 9.60%, C7H5Cl5N3O2P3 (432) requires C 19.49, H 1.16, N 9.7%).

# 4.3. Synthesis of 1,1,3,3,5-pentahydroxypyrene -5-(4-formylphenoxy)cyclotriphosphazatriene (**2**)

Compound **1**, (0.21 g, 0.48 mmol) and 1-hydroxypyrene (0.63 g, 2.92 mmol) were dissolved in dry THF (10 mL) under argon atmosphere. After stirring for 15 min at 40  $^{\circ}$ C, dry and finely powdered caesium carbonate (1.42 g, 4.38 mmol) was added. The reaction mixture was stirred under argon atmosphere at 60  $^{\circ}$ C for

24 h. The reaction mixture was filtered and the volume was evaporated under vacuum and the product was purified by preparative TLC on silica gel using hexane: THF (2:1) as the eluent. Compound (**2**) was isolated as a brown solid. Yield: 0.36 g (55%); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 6.6-6.7$  (m, 4H, ArCH),  $\delta = 6.98-8.12$  (m, 45H, ArCH),  $\delta = 9.02$  (s, 1H, -CHO).{<sup>1</sup>H}<sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 9.59$  [2P, >P(OPyrene)<sub>2</sub>, A<sub>2</sub>], 7.94 [1P > P(OPyrene)(OPhCHO),B], <sup>2</sup>J<sub>P,P</sub> = 90.04 Hz, MS (MALDI-TOF) m/z (%):1342 (100) [M + H]<sup>+</sup>. Elemental analysis: (found: C 78.15, H 3.08, N 3.60%, C<sub>87</sub>H<sub>50</sub>N<sub>3</sub>O<sub>7</sub>P<sub>3</sub> (1341) requires C 77.85, H 3.75, N 3.13%).

# 4.4. Synthesis of 1,1,3,3,5-pentahydroxypyrene -5-(BODIPY) cyclotriphosphazatriene (**3**)

2,4-Dimethyl pyrrole (5.84 mmol, 556 mg) and compound **2** (0.2 mmol, 268 mg) were dissolved in 50 mL absolute  $CH_2Cl_2$  (argon gas was bubbled through  $CH_2Cl_2$  for 30 min) under argon atmosphere. One drop of trifluoroaceticacid (TFA) was added and the solution stirred at room temperature nearly 3–4 h. At this point, a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (0.2 mmol, 48 mg) in absolute  $CH_2Cl_2$  (10 mL) was added, stirring



**Fig. 3.** Electronic absorption spectra of (A) compounds **2**, **3**, **5** and (B) compounds **2**, **4** and **6** in dichloromethane.

was continued for 30 min followed by the addition of Et<sub>3</sub>N (1 mL) and BF<sub>3</sub>.Et<sub>2</sub>O (1 mL). The reaction mixture filtered off and the reaction mixture was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by preparative TLC on silica gel using hexane: THF (3:2) as the eluent. Compound (**3**) was isolated as an orange solid (68 mg, 22%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta = 1.57$  (m, 6H, CH<sub>3</sub>),  $\delta = 2.21$  (m, 6H, CH<sub>3</sub>),  $\delta = 5.78$  (m, 2H, –CH),  $\delta = 6.7-6.8$  (m,4H, ArCH),  $\delta = 6.96-8.22$  (m, 45H, ArCH),; {<sup>1</sup>H}<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta = 155.3$ , 143.3141.7, 131.1, 129.4, 127.8, 125.9, 124.6, 121.1, 116.3, 14.5. {<sup>1</sup>H}<sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta = 9.53$  [2P, >P(OPyrene)<sub>2</sub>, A<sub>2</sub>], 8.40 [1P > P(OPyrene)(OBODIPY),B], <sup>2</sup>J<sub>P,P</sub> = 90.54 Hz, MS (MALDI-TOF) *m*/*z* (%):1560 (100) [M + H]<sup>+</sup>. Elemental analysis: (found: C 76.55, H 4.08, N 4.58%, C<sub>99</sub>H<sub>63</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>6</sub>P<sub>3</sub> (1559) requires C 76.21, H 4.07, N 4.49%).

# 4.5. Synthesis of 1,1,3,3,5-pentahydroxypyrene-5-(monostyrylBODIPY)cyclotriphosphazatriene (**4**)

Compound (3) (60 mg, 0.04 mmol) and dimethylaminobenzaldehyde (12 mg, 0.08 mmol) were heated under reflux in a mixture of toluene (5 mL), glacial acetic acid (0.3 mL), piperidine (0.4 mL) and small amount of Mg(ClO<sub>4</sub>)<sub>2</sub>. Any water formed during the reaction, was removed azeotropically upon heating overnight in a Dean-Stark apparatus. Crude product concentrated under vacuum, then purified by preparative TLC on silica gel using hexane: dichloromethane (1:3) as the eluent. The blue coloured fraction (4) was collected and the solvent was removed under reduced pressure to yield the desired material (**4**) (13 mg, 21%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.98–8.18 (m, 45H, ArCH), 7.48–7.50 (m, 2H), 7.24 (s, 1H), 7.21 (d, 1H, *J* = 16.3), 7.18 (d, 1H, *J* = 16.3), 7.11 (d, 2H, *J* = 8.1), 6.90 (d, 2H, J = 7.9), 6.65 (d, 2H, J = 8.1), 6.58 (s, 1H), 2.99 (s, 6H), 2.59 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H);  ${}^{1}$ H ${}^{13}$ C NMR (CDCl<sub>3</sub>)  $\delta$  = 161.0, 155.8, 143.2, 139.6, 138.4, 131.1, 129.3, 128.8, 125.2, 124.1, 122.1, 121, 117.9, 116.1, 54.9, 14.5, 14.3, 13.1;  ${}^{1}H{}^{31}P$  NMR (CDCl<sub>3</sub>)  $\delta = 9.55$  [2P,  $>P(OPyrene)_2$ , A<sub>2</sub>], 8.41 [1P > P(OPyrene)(OBODIPY),B], <sup>2</sup>J<sub>PP</sub> = 66.96 Hz, MS (MALDI-TOF) m/z (%): 1692 (100) [M + H]<sup>+</sup>. Elemental analysis: (found: C 76.75, H 4.38, N 4.90%, C<sub>108</sub>H<sub>72</sub>BF<sub>2</sub>N<sub>6</sub>O<sub>6</sub>P<sub>3</sub> (1691) requires C 76.69, H 4.29, N 4.97%).



**Fig. 4.** Absorption and emission spectra of donor–acceptor (compounds **2**, **5** and **6**, respectively) in dichloromethane. Yellow (for compound **3**) and pink (for compound **4**) coloured region is the spectral overlap between the fluorescence spectrum of donor and absorption spectrum of acceptor. Excitation wavelength = 345 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

# 5. Results and discussion

### 5.1. Synthesis and structural characterization

In this work, the synthetic procedures for preparation of the compounds are shown in Scheme 1. Hexachlorocyclotriphosphazene was reacted with excess 4-hydroxybenzaldehyde in the presence of potassium carbonate in THF to yield 1,1,3,3,5-pentachloro-5-(4-formylphenoxy)cyclotriphosphazatriene (1). Compound 2 was synthesized by treating compound 1 with excess of 1-hydroxypyrene in the presence of caesium carbonate in THF at 60 °C. Both cyclic phosphazenes (1 and 2) were characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, mass spectrometry (MALDI-TOF techniques) and elemental analysis and these data are presented in Section 2.

The aldehyde substituted cyclotriphosphazene (**2**) was then used in the usual manner [26] in the synthesis of a BODIPY dye by reaction with 2,4-dimethylpyrrole in the presence of TFA and DDQ, followed by the addition of  $BF_3.Et_2O$ . The crude product was subjected to column chromatographic purification and afforded the desired pure compound **3** as an orange solid in 22% yield. The



Fig. 5. Emission spectra of (A) 2, 3, 5 and (B) 2, 4, 6 in dichloromethane. Excitation wavelength = 345 nm.

product was characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR and mass spectrometry. The molecular ion peaks at 1560.3 in the matrixassisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum confirmed the compound **3** (Fig. 1s-a). The protondecoupled <sup>31</sup>P NMR spectrum of compound **3** displays the expected A<sub>2</sub>B spin system (Fig. 2s-a). The resonances belonging to phosphorous atoms were observed at ca. 9.53 ppm for P(OPvrene)<sub>2</sub> and at ca. 8.40 ppm for P(OPvrene)(O-BODIPY). Compound **3** was condensed with 4-dimethylaminobenzaldehyde in the presence of piperidine to give the compound **4** as blue solid in 21% yield. This Knoevenagel reaction was inspired by previous work [25]. As would be expected by the type of condensation employed, an *E* conformation of the double bond was found as revealed by the observed J = 16.3 Hz proton-proton coupling constant in the proton NMR spectra [27]. The molecular ion peaks at 1692.5 in the MALDI-TOF mass spectrum confirmed the compound **4** (Fig. 1s-b). The proton-decoupled <sup>31</sup>P NMR spectrum of compound **3** is shown as the expected A<sub>2</sub>B spin system (Fig. 2s-b). The resonances belonging to phosphorous atoms were observed at ca. 9.55 ppm for P(OPyrene)<sub>2</sub> and at ca. 8.41 ppm for P(OPyrene)(O-styryl-BODIPY). Although compounds **3** and **4** have similar spectra, the magnitude of the  ${}^{2}I$  (PP) is different for these compounds, viz. 90.54 Hz for compound (3), and 66.96 Hz for compound 4. In addition, the elemental analysis results, <sup>1</sup>H and <sup>13</sup>C NMR data for the newly synthesized cyclic phosphazene derivatives (1-4) were consistent with the assigned formulations (see Section 2).

# 6. Photo-physical properties

### 6.1. Electronic absorption spectrum

The absorption spectra of **2–6** were recorded in dichloromethane and are shown in Fig. 3A, B. Compound **3** shows two major characteristic absorption bands at 344 and 503 nm (Fig. 3A). The spectrum of the compound **3** exhibits similar features to other pyrene compounds with a maximum absorption wavelength at 344 nm, corresponding to the  $S_0 \rightarrow S_2$  transition of pyrene [6,7]. The absorption band at ca. 500 nm is attributed to the lowest energy spin-allowed  $\pi-\pi^*$  transition of the BODIPY moiety [28]. Similarly, the electronic spectrum of the compound **4** displays two major characteristic absorption bands at 344 and 610 nm (Fig. 3B). In the absorption spectra of both **3** and **4**, there are two distinct absorbance peaks indicating that there are two non-interacting chromophores in each compound with no-ground state interaction (Fig. 3A, B).

# 6.2. Fluorescence spectra

The fluorescence emission spectra of compound **3** and **4** were recorded with an excitation wavelength of 345 nm in dichloromethane at room temperature. In the cases where two different dyes were used, the relative proximity of the two moieties and an overlap of the emission maximum of one dye with the absorption maximum of the other dye may result in fluorescence resonance energy transfer (FRET) [29,30]. Fig. 4 illustrates the spectral overlap between the fluorescence spectrum of donor (2) and absorption spectrum of acceptor (5 and 6). Therefore, the compounds 3 and 4 constitute a potential donor-acceptor pair in energy transfer. In order to obtain more information about the energy transfer, the emission spectrum of compound 3 with the emission spectra of their reference compounds 2 and 5 were measured under the same conditions (5  $\times$  10<sup>-7</sup> mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{exc}$  345 nm) and are shown in Fig. 5A. In the emission spectrum of compound **3** excited from pyrene at 345 nm, there is significant quenching of donor emission at around 460 nm and enhancement in acceptor emission at around 517 nm. In addition to that, compound **5** excited at 345 nm has very weak emission at around 510 nm (Fig. 5A). In the emission spectrum of compound **4** excited from pyrene at 345 nm, similar results were obtained. There is a significant quenching of donor emission at around 460 nm and enhancement in acceptor emission at around 685 nm. Additionally, compound **6** displays only a very weak and broad emission peak around 680 nm (Fig. 5B). This shows that all increase in emission at 510 nm is coming from energy transfer from donor groups (Fig. 5A, B). The fluorescence quantum yield of 2 in DCM is 0.454, while that of the compounds 3 and 4 greatly dropped to 0.0015 and 0.0013, respectively. According to Eq. (2), the energy transfer quantum yield values of **3** and **4** were estimated. The  $\Phi_{\rm ENT}$  values were found ~0.99 for compound **3** and 0.86



**Fig. 6.** Absorption (blue) and emission (red) spectra of compound **4** in dichloromethane. The inset shows absorption (blue) and emission (red) spectra of reference compound **6**. Excitation wavelength = 345 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for compound **4**, showing that this is a very efficient energy transfer process in **3** and **4**. Stokes' shift which is the difference between the maximum of the lowest energy absorption band and the maximum of emission band was found to be larger for compounds **3** and **4** compared with their reference compounds **6** and **7**. As an example, the overlay of absorption and emission spectra of compound **4** is shown in Fig. 6, and the inset shows that for the corresponding reference compound **6**. It is clear from Fig. 6 that the compound **4** exhibits 75 nm Stokes' shift compared with 55 nm Stokes' shift observed for compound **6**. Thus, the larger Stokes' shifts observed for compounds **3** and **4** may be advantageous for their potential applications in direct multicolor labeling experiments.

# 7. Conclusion

In summary, the design and synthesis of compounds **3** and **4** which contain both BODIPY and pyrene chromophore groups linked to each other by a cyclotriphosphazene core was accomplished. All compounds were fully characterized by standard spectroscopic techniques. The photophysical behavior of all compounds was studied by UV–Vis absorption and fluorescence spectroscopies. Our compounds exhibit a highly efficient energy transfer, which is due to the good spectral overlap between the emission of energy donor moiety and the absorption of energy acceptor moiety. The compounds exhibit relatively large Stokes' shifts with quantum yields comparable to their respective BODIPY precursors. This type of cyclophosphazene appended with fluorophores may have potential applications in organic light emitting diodes and light harvesting arrays and as fluorescent labels [31,32].

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.07.022.

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