NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Journal Name

RSCPublishing

ARTICLE

Synthesis and Use of "Clickable" Bay-region Tetrasubstituted Perylene tetracarboxylicacid tetraesters and a Perylene monoimide diester as Energy Acceptors

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Edanur Aydin,[a] Bilal Nisanci, [a] Murat Acar, [a] Arif Dastan, [a] and Özgür Altan Bozdemir* [a]

Bay-region chlorine- or phenoxy- substituted two novel perylene tetracarboxylic tetrapropargylesters (PTTEs) and a phenoxy- substituted perylene monoimide dipropargylester (PMIDE) were synthesized, photophysically characterized, and decorated with energy donating coumarin chromophores by means of microwave-assisted Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions.

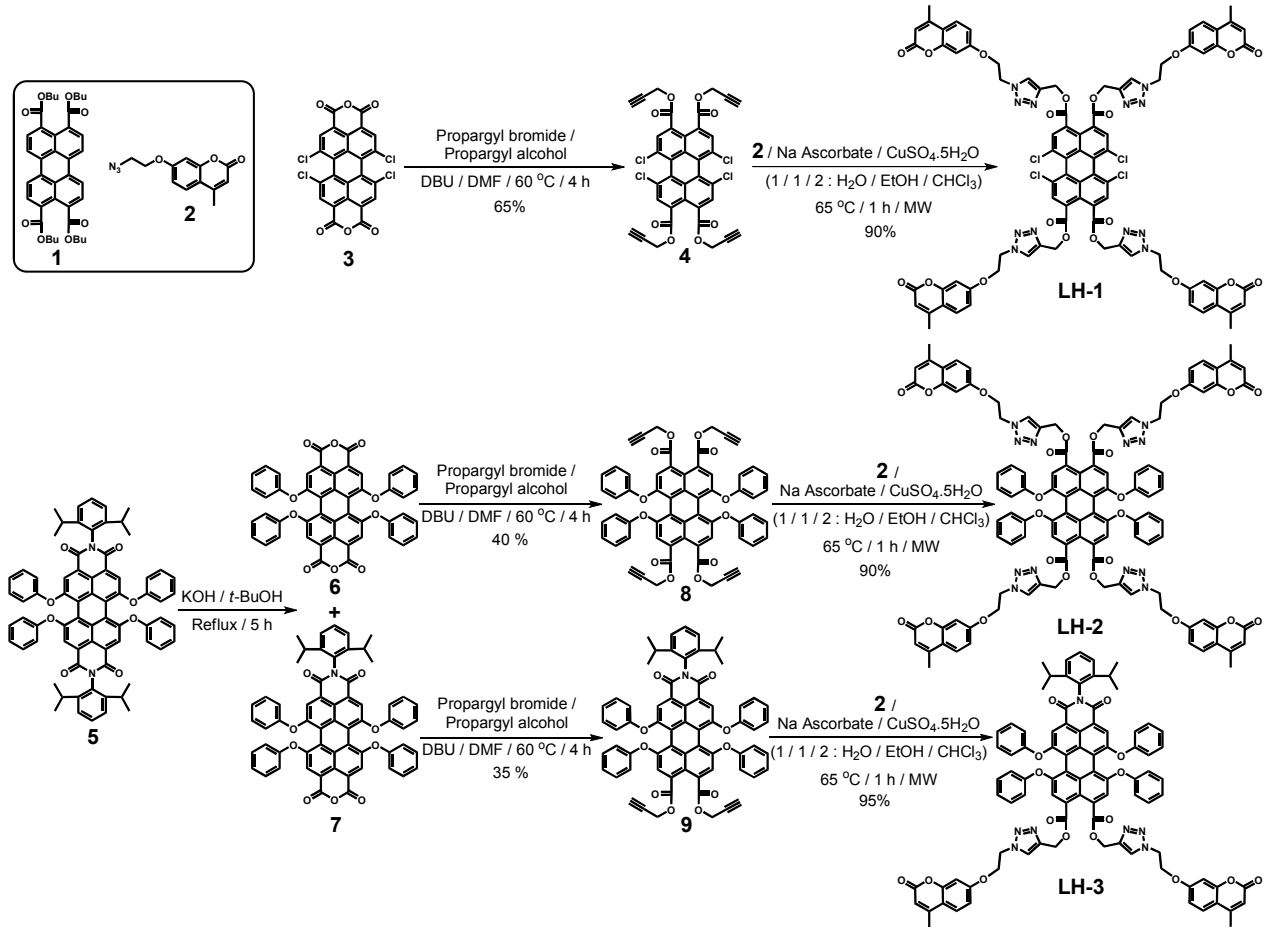
Introduction

In recent years, perylene tetracarboxylic tetraesters (PTTEs), being close relatives of perylene bisimide (PBI) dyes, have attracted great attention among researchers on account of their high absorption coefficients in the visible region and their good fluorescence properties.[1,2] The much better solubility of bay-region-unsubstituted PTTEs in common organic solvents, comparing to that of similar PBIs, allows for facile purifications and easy functionalization at the bay-region by means of bromination and nitration.[1] Subsequent nucleophilic aromatic substitution or transition metal-catalyzed coupling reactions carried out on these derivatives have opened up novel pathways for the synthesis of more extended aromatic structures.[2] In addition to these types of applications, their high propensity for self-aggregation into one-dimensional supramolecular polymers and columnar liquid crystals has also been demonstrated.[3] Currently used PTTE derivatives bear one or two substituents at the bay-region[2] and more recently, a couple of derivatives with four chlorine atoms were employed as intermediates *en route* to other perylene structures.[4] It is obvious that increasing the number of substituents placed at the bay-region would be an important contribution to the chemistry of this class of fluorescent dyes as it may lead to improved photophysical properties. Another interesting structure possessing a perylene skeleton is the perylene monoimide diester (PMIDE).[5] As the electron withdrawing ability of these compounds lie in between PBIs and PTTEs, they have the potential of being implemented for the fine tuning of device performances in novel nanoelectronic devices.

The development of artificial systems capable of collecting and transferring light energy into suitable energy absorbing sites continues to be the subject of a great number of research activities pursuing the ultimate goal of mimicking Nature's photosynthetic reaction centers and of the production of efficient solar energy concentrators.[6] The efficient transfer of solar energy in the form of electronic energy transfer (EET) can be accomplished with systems consisting of rationally designed energy donor and energy acceptor chromophores. In this manner, dendrimers offer one of the most efficient synthetic structures for the arrangement of energy donor chromophores around energy acceptors so as to channel the light energy after its collection from a light source. To date, several light-harvesting dendrimers have been synthesized by exploiting well-known dye molecules,[7] among which several members of rylene dyes played important roles both as energy donors and acceptors.[8] However, to the best of our knowledge, although there is an example for the use of perylenetetraesters in light harvesting dendrimers,[8g] bay-region tetrasubstituted PTTE and PMIDE derivatives have never been considered as acceptor cores in dendritic energy transfer systems. In this study for the first time, two novel tetrasubstituted PTTE derivatives and a PMIDE derivative with propargyloxy ester functionalities were constructed to explore their behaviors as energy acceptors in light-harvesting systems

Results and discussion

In the construction of target light harvesters, we employed a convergent approach to attach well-known 4-methyl-7-alkoxycoumarin energy donor chromophore *via* microwave assisted Cu(I)-catalyzed 1,3-dipolar cycloaddition, relying on the fact that the "Click chemistry" has been one of the most reliable means for the synthesis of dendrimers.[9] As shown in the Scheme 1, our synthetic studies commenced with the synthesis of the first core energy acceptor molecule 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylicpropargyl ester **4**. 1,6,7,12-tetrachloroperylenetetracarboxylic acid dianhydride **3** was reacted with a mixture of propargyl bromide and propargyl alcohol in DMF at 60 ^{o}C in the presence of a strong base DBU. In the last step, this alkyne-functionalized PTTE **4** and compound **2** were reacted in a microwave reactor in a solvent mixture (1/1/2:H_2O/EtOH/$CHCl_3$) at 65 ^{o}C in the presence of sodium ascorbate and $CuSO_4$ for 1 h, affording **LH-1** in 90%



Scheme 1. Synthesis of propargyllated perylene derivatives and their conversion into light harvesting systems **LH-1**, **LH-2**, and **LH-3**

yield after chromatographic purifications. To obtain our phenoxy substituted longer wavelength light-harvesting structures **LH-2** and **LH-3**, we first synthesized the tetraphenoxy- perylene bisimide **5** by following a literature procedure.[3d] Accordingly, the partial basic hydrolysis reaction was carried out in the presence of KOH in a water/t-butanol mixture at reflux temperature for 5 h.[10] This reaction, after acidic work-up, apart from the starting material, resulted in the formation of dianhydride **6** and monoimide-monoanhydride **7** as a mixture which was directly used in the next step without further purification. Following the same protocol, this mixture was reacted with a mixture of propargyl bromide and propargyl alcohol in DMF at 60 °C for 4 h in the presence of DBU. After chromatographic purifications, perylene tetraphenoxy tetrapropargyl ester **8** and perylene tetraphenoxy monoimide bispropargyl ester **9** were obtained in 40% and 35% yields from **5**, respectively. Employing the same microwave assisted alkyne-azide cycloaddition reactions between compound **2** and **8** and **2** and **9** in final steps resulted in the formation of **LH-2** and **LH-3**. After chromatographic purifications, each target molecule was obtained in 90% and 95% yields, respectively.

It should be noted that among the perylenetetracarboxylic acid derivatives, PTTEs are the weakest electron acceptors as a result of the poor orbital interactions between ester carbonyls and the perylene ring comparing to the imide carbonyls of PBIs. PMIDEs, on the other hand, are stronger electron acceptors than PTTEs while they are weaker than PBIs. Accordingly, absorption and emission wavelength maxima of these compounds follow the same trend; PTTEs being the shortest wavelength absorbers and emitters. One of the strategies frequently employed in order to shift the absorption and emission maxima of fluorescent dyes to the red end of the visible spectrum is to attach electron donating functionalities at suitable positions to achieve maximum conjugation. If we take the perylene-3,4:9,10-tetra(n-butoxy)tetracarboxylicacid tetraester **1** as the parent PTTE molecule (λ_{abs} = 471 nm, λ_{ems} = 516 nm) for our comparisons, it is obvious that substituents at the bay region would increase the solubility of resulting compounds and depending on the electron withdrawing or releasing abilities, they would alter the absorption and emission maxima of PTTEs (Table 1). As expected, a hypsochromic shifting in absorption and emission maxima for compound **4** (λ_{abs} = 459 nm, λ_{ems} = 499 nm) was observed due to the presence of electron withdrawing chlorine substituents, while a bathochromic shifting was detected for **8** (λ_{abs} = 492 nm, λ_{ems} = 534 nm) due to the attachment of electron releasing phenoxy substituents. For PMIDE **9**, it is not surprising that the presence of only one imide group is sufficient to endow longer wavelength absorption and emission maxima (λ_{abs} = 540 nm, λ_{ems} = 572 nm) comparing to PTTEs.

In order to assess the efficiency of electronic energy transfer, several steady-state and time-resolved spectroscopic measurements were carried out on each light-harvesting system (Table 1, Fig. 1, Fig. 2, and the ESI Fig. 1-6). The absorption spectrum of **LH-1** appears as a summation of transitions emanating from coumarin **2** and PTTE **4** (ESI Fig. S1).

Table 1. Photophysical data for the compounds.

Compound[a]	λ_{abs} (nm) / ε_{max} ($M^{-1}cm^{-1}$)	λ_{ems} (nm)	τ (ns) / λ_{exc} (nm)	χ^2	Φ_F / λ_{exc} (nm)	J / $10^{14}M^{-1}cm^{-1}nm^4$	R_o (nm)	E (%)	$k_T(r)/ns^{-1}$
1	471 (32410)	516	3.6 (457)	1.08	1.00[b] (450)				
2	320 (10968)	378	0.6 (337)	0.98	0.09[c] (315)				
4	459 (18587)	499	1.8 (457)	0.91	0.16[b] (450)				
					0.04[c] (315)				
LH-1	459 (18744)	499	1.5 (337)	0.95	0.10[c] (315)	1.86	2.46	90	16.4
8	492 (29180)	534	5.7 (457)	1.05	0.57[b] (496)				
					0.20[c] (315)				
LH-2	492 (29265)	534	5.4 (337)	0.95	0.25[c] (315)	2.54	2.54	93	22.0
9	540 (20853)	572	5.9 (500)	0.93	0.30[b] (496)				
					0.07[c] (315)				
LH-3	540 (20679)	572	5.4 (337)	1.01	0.10[c] (315)	1.73	2.43	87	11.4

[a]All spectra were recorded in dilute solutions in $CHCl_3$. [b] 0.1 M aqueous Fluorescein solution (Φ_F = 0.95) was used as reference.[c]0.5 M aqueous Quinine sulfate solution (Φ_F = 0.55) was used as reference. λ_{abs} / λ_{ems}: Maximum absorption / emission wavelengths. λ_{exc}: Excitation wavelength. τ: Fluorescence lifetime. Φ_F: Fluorescence quantum yield. R_o: Förster distance. J: Spectral overlap integral. E: Energy transfer efficiency. $k_T(r)$: Energy transfer rate constant..

That an efficient electronic energy transfer takes place between coumarin donors and PTTE acceptor unit upon excitation of peripheral chromophores at 315 nm is evident from the near complete quenching of coumarin centered fluorescence at 378 nm, comparing to the emission from the model compound **2** with an equal absorption intensity (Fig.1a). Also, a comparison of the emission intensity of **LH-1** at 499 nm with the PTTE **4** reveals a 10-fold increase, demonstrating a powerful antenna effect (Fig.1a). It should be noted here that this donor unit, with a quantum yield of less than 1%, can be referred to as a "dark donor"; however, when it is excited, the excitation energy is transferred to the acceptor faster than the other quenching pathways.[11]

Similar measurements were carried out for **LH-2**, as well. In this system, absorption features characteristic of **2** and PTTE **8** are observed in the absorption spectrum (ESI Fig. S2). The excitation into the coumarin part at 315 nm resulted in a strong fluorescence with nearly 3.1-fold increase in the emission intensity at 534 nm comparing to the reference dye PTTE **8** emission, which was accompanied by a complete quenching of the coumarin part (Fig. 1b). This somewhat smaller increase in the acceptor emission is due to the presence of vibronic transitions observed at higher energies in PTTE **8** and **LH-2** (300–350 nm region) leading to a relatively intense fluorescence emanating from the possibility of direct excitation of the PTTE part in **LH-2** at 315 nm.

In **LH-3**, where only two donor coumarin units are present, absorption spectrum is again a combination of transitions from coumarin **2** and PMIDE **9** units, covering a broad wavelength range stretching from nearly 600 nm to 200 nm (ESI Fig. S3). It is appearent that the excitation of **LH-3** at 315 nm leads to an increased fluorescence at 572 nm as a result of an energy transfer revealing itself as a 2.4-fold enhanced fluorescence as compared to the emission intensity of the reference dye PMIDE **9** at equal concentrations (Fig. 1c).

In order to investigate the likelihood of the intermolecular energy transfer between the components of light-harvesters and to confirm that the observed energy transfer is intramolecular in nature, suitable donor-acceptor mixtures – representing each light-harvester as a combination of separate entities – were prepared and subjected to the same spectroscopic measurements (ESI Fig. S4-S6). Hence, the excitation of mixtures of donor and acceptor molecules **2** and **4**, **2** and **8**, and **2** and **9** at the donor absorption maximum (315 nm) revealed no intermolecular energy transfer between individual chromophores as evidenced by the low intensity of acceptor emissions in each case and the absence of coumarin quenching.

Table 1 gives valuable photophysical parameters which can be used in the estimation of the efficiency of energy transfer in all light-harvesting systems obtained in this study: acceptor emission lifetimes (τ) and fluorescence quantum yields (Φ_F) increase comparing to each acceptor model compounds when excited at the donor site (315 nm), whereas donor lifetimes and quantum yields decrease nearly to zero, indicating the electronic energy transfer. The fluorescence decays of **LH-1**, **LH-2**, and **LH-3** (ESI Fig. S19-S26) were found to be single-exponential with χ^2 values smaller than 1.2, as a sign for a good fit. The Förster radii (Ro) determined for all compounds are very close to each other as predicted from their structural similarity. Due to the close proximity of donor and acceptor units, fast energy transfer rates (k(r)) were calculated based on the fluorescence intensity data for **LH-1**, **LH-2**, and **LH-3**, and the values are 1.64 x 10^{10} s^{-1}, 2.20 x 10^{10} s^{-1}, and 1.14 x 10^{10} s^{-1}, respectively. The energy transfer efficiencies were then calculated as 90% for **LH-1**, 93% for **LH-2**, and 87% for **LH-3**.

One of the possible pitfalls of using donor quantum yields and lifetimes in calculating energy transfer efficiencies is the preassumption that the changes in these values are merely related to the intramolecular energy transfer taking place between the donor and acceptor chromophors, ignoring the other common quenching pathways. In order to correctly determine the energy transfer efficiency, one has to compare the absorption and excitation spectra of the light-harvesting system – normalized at the acceptor absorption wavelength maximum – over the entire spectral range, in order to be sure that the harvested photons by the donor are quantitatively transferred to the acceptor unit. Indeed, this way of determining energy transfer efficiency has proven more reliable by many researchers as it gives directly the ratio of the number of photons absorbed by the donor molecules to the number of excitations generated in the acceptor.[12]

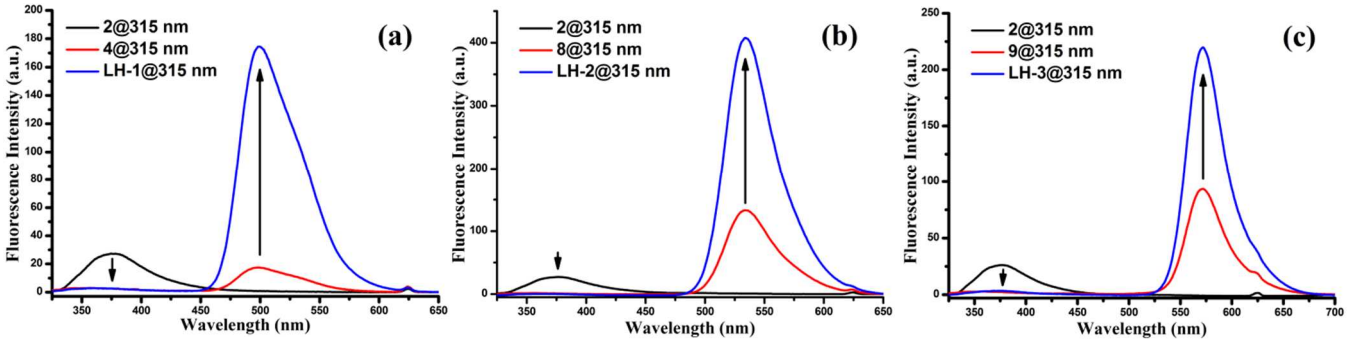


Fig. 1 (a) Fluorescence emission spectra of compounds **2**, **4** and **LH-1** upon excitation at 315 nm in $CHCl_3$. The concentrations of compounds **2** and **4** were adjusted so that they have equal absorbances at 320 nm and 459 nm with **LH-1**. (b) Fluorescence emission spectra of compounds **2**, **8** and **LH-2** upon excitation at 315 nm in $CHCl_3$. The concentrations of compounds **2** and **8** were adjusted so that they have equal absorbances at 320 nm and 492 nm with **LH-2**. (c) Fluorescence emission spectra of compounds **2**, **9** and **LH-3** upon excitation at 315 nm in $CHCl_3$. The concentrations of compounds **2** and **9** were adjusted so that they have equal absorbances at 320 nm and 540 nm with **LH-3**.

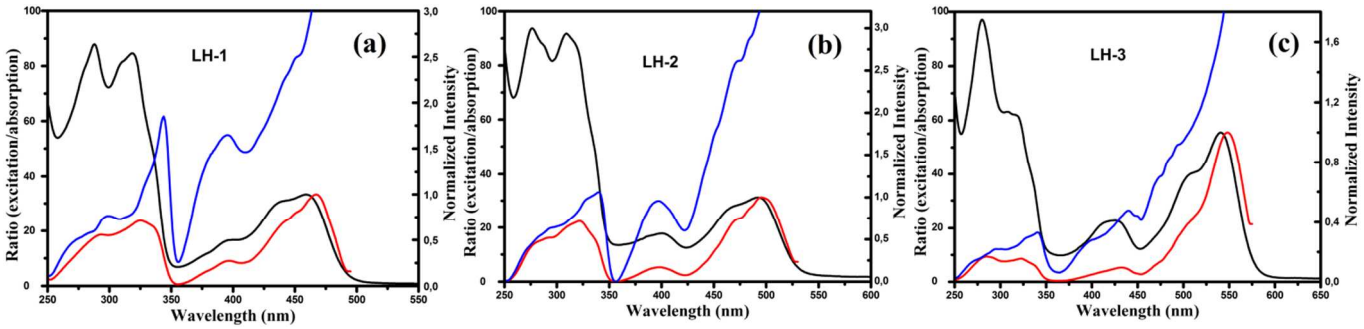


Fig. 2 Absorption (black) and excitation (red) spectra of (a) **LH-1**, (b) **LH-2**, and (c) **LH-3,** normalized at the absorption maxima of the core acceptor units (459 nm for **LH-1**, 492 nm for **LH-2**, and 540 nm for **LH-3**). Blue lines represent the efficiency of the percent energy transfer as a function of the excitation wavelength.

When we applied this method to our light-harvesting systems, in each case, we observed a poor match between the excitation – acquired for the respective acceptor emission maximum – and donor absorption region of the spectrum (Fig. 2). In contrast to the values calculated by means of donor quantum yields and lifetimes, we determined 25%, 24%, and 13% efficiency of energy transfer for **LH-1**, **LH-2**, and **LH-3**, respectively. Similar to the many other dendritic light harvesters constructed by means of flexible bonding units,[12b] these low values must be due to the presence of various nonradiative quenching pathways in these conformationally flexible supramolecules, as we did not observe any aggregation or photodecomposition in these systems after several fluorescence measurements. Nevertheless, upto 10-fold fluorescence intensity increments in the presence of coumarin donor groups can safely be regarded as a sign of an efficient transfer of energy within these light-harvesters.

Conclusions

In summary, we demonstrated here that the bay-region tetrasubstituted perylene tetraester and perylene monoimide diester derivatives can be prepared with reactive ester functionalities which are ready to be exploited in the construction of various functional supramolecular systems such as light-harvesting dendrimers or biolabels, by employing a fast, microwave-assisted click chemistry. As evaluated by various spectroscopic techniques, excitation energy can be channeled into these novel dyes when they take part in light-harvesting systems and they have the potential of being used as donor sites if suitable donor-acceptor combinations are designed. Additionally, self aggregation abilities and liquid crystallinity properties are other important features of these derivatives, on which our works are in progress.

Experimental

General

Compounds **2**[13] and **3**[14] were synthesized following the procedures reported in the literature. All chemicals and solvents purchased from Sigma-Aldrich were used without further purification. All solvents were dried and distilled before use. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F_{254} and the plates were inspected by 254 nm UV-light and/or by acquiring ^{1}H-NMR spectra. Column chromatography was performed over Merck Silica gel 60F (70-230 mesh ASTM). The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian-400 or a Bruker-400 spectrometer in $CDCl_3$ using tetramethylsilane as the internal reference. All spectra were recorded at 25 ^{o}C and coupling constants (*J* values) are given in Hz. Chemical shifts are given in parts per million (ppm). Abbreviations used to define multiplicities are as follows: s = singlet; d = doublet; t = triplet; q = quartet; hept = heptet; m = multiplet; br = broad. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Microwave reactions were performed in a CEM Discover

LabMate 200W microwave reactor. Absorption spectrometry was performed using a Shımadzu spectrophotometer. Steady-state fluorescence measurements were conducted using a Shımadzu RF-5301PC spectrofluorometer. Fluorescence decays for the lifetime measurements were carried out by means of a LaserStrobe Model TM-3 lifetime fluorophotometer from Photon Technology International (PTI).

Photophysical calculations: Quantum yield measurements and calculations were done using Fluorescein (Φ_F = 0.95, 0.1 M aqueous solution) and Quinine sulfate ((Φ_F = 0.55, 0.5 M aqueous solution) as standard dyes. Following formula was used for calculations:

$$\Phi = \Phi_R \left(\frac{I}{I_R}\right)\left(\frac{n^2}{n_R^2}\right)\left(\frac{1-10^{OD_R}}{1-10^{OD}}\right)$$

where **Φ** is fluorescence quantum yield, I is the integrated fluorescence intensity, n is the refractive index of solvent, and OD is the optical density (absorption). The subscript R refers to the reference fluorophore of known quantum yield.[S3]

Förster distances (R_o), energy transfer efficiencies (E), and energy transfer rate constants ($k_T(r)$) were calculated using forlmulae below: [15]

$$R_0 = 0.211\left(K^2 n^{-4} \Phi_D J_{(\lambda)}\right)^{1/6} \qquad (in\ Å)$$

$$E = 1 - \frac{F_{DA}}{F_D} = \frac{R_0^6}{R_0^6 + r^6}$$

$$k_T(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

where R_o stands for the Förster distance, $\boldsymbol{\Phi_D}$ is the quantum yield of the donor in the absence of acceptor, n is the refractive index of the medium, r is the distance between the donor and acceptor, and τ_D is the lifetime of the donor in the absence of acceptor. K^2 is usually assumed to be equal to 2/3. The overlap integral (J(λ)) expresses the degree of spectral overlap between the donor emission and the acceptor absorption, $\boldsymbol{k_T(r)}$ is the rate of energy transfer from donor to acceptor.

Syntheses

Synthesis of Compound 4: 1,8-Diazabicyclo[5,4,0]undec-7-en (114 µL, 0.76 mmol) and propargyl alcohol (88 µL, 1.52 mmol) were added to a stirred solution of 3 (100 mg, 0.19 mmol) in DMF (3.5 mL) at 60 °C and the mixture was stirred 30 min. Then, a solution of propargyl bromide (80% in toluene, 115 µL, 1.52 mmol) in DMF (0.5 mL) was added dropwise and the solution was stirred for 3 h at the same temperature. After the completion of the reaction, the crude product was precipitated in water (50 mL) and the solid was filtered by using a G4 glass filter. The solid obtained was dissolved in CH_2Cl_2 (30 mL) and washed with water (2 x 10 mL) and brine. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by thin layer chromatography (TLC) with CH_2Cl_2 to afford 4 as a yellow solid (91 mg, 0.13 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.20 (s, 4H), 5.04–4.99 (m, A part of the AB system, 4H), 4.97 (dd, B part of the AB system, *J* = 15.6, 2.4 Hz, 4H), 2.61 (t, *J* = 2.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 166.2, 134.1, 133.0 (2C), 129.5, 127.8, 123.3, 76.9, 76.3, 53.8. HR-ESI-MS: *m/z* Calcd: 715.9599; found: 715.9590.

Synthesis of LH-1: Compound 4 (50 mg, 0.07 mmol), 2 (134 mg, 0.55 mmol), $CuSO_4.5H_2O$ (17 mg, 0.07 mmol) and sodium ascorbate (7.4 mg, 0.04 mmol) were dissolved in a solvent mixture of $CHCl_3$ (2 mL) / EtOH (1 mL) / H_2O (1 mL) in a microwave reaction vial. The reaction mixture was stirred under microwave irridation at 65 °C for 1 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by thin layer chromatography (TLC) (MeOH:CH_2Cl_2 :7%) to afford LH-1 as a yellow solid (105 mg, 0.07 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.10 (s, 4H), 8.05 (s, 4H), 7.42 (d, *J* = 8.7 Hz, 4H), 6.82–6.76 (m, 8H), 6.08 (s, 4H), 5.48 (d, A part of the AB system, *J* = 12.7 Hz, 4H), 5.44 (d, B part of the AB system, *J* = 12.7 Hz, 4H), 4.85 (t, *J* = 5.0 Hz, 8H), 4.45 (t, *J* = 5.0 Hz, 8H), 2.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 166.4, 160.9, 160.5, 155.0, 152.3, 142.1, 133.6, 132.6, 129.7, 127.3, 126.0, 125.6, 122.9, 114.3, 112.4, 112.0, 101.8, 66.6, 59.2, 49.6, 18.6. HR-ESI-MS: *m/z* Calcd: 1696.2801; found: 1696.2784.

Syntheses of Compounds 8 and 9: A solution of KOH (4.8 g, 85.5 mmol) in H_2O (2 mL) was added dropwise to a stirred solution of compound 5 (480 mg, 0.44 mmol) in isopropanol (30 mL) and the mixture was stirred at 85 °C for 5 h. The dark green reaction mixture was cooled to room temperature and glacial acetic acid (50 mL) was added. The mixture was stirred for an additional 1 h at 50 °C. The crude product was precipitated in water (50 mL) and the solid was collected using G4 glass filter, washed with water (3 x 10 mL) and dissolved in CH_2Cl_2 (30 mL). The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. This product was used in the next step without further purification. 1,8-Diazabicyclo[5,4,0]undec-7-en (299 µL, 2.00 mmol) and propargyl alcohol (230 µL, 4.00 mmol) were added to a stirred solution of the above mixture (430 mg) in DMF (7 mL) at 60 °C. After stirring for 30 min at 60 °C, a solution of propargyl bromide (80% in toluene, 303 µL, 4.00 mmol) in DMF (1 mL) was added and the reaction mixture was stirred for 3 h at the same temperature. The crude product was precipitated in water (150 mL) and the solid was filtered by G4 glass filter. The solid residue was washed with water (3 x 10 mL), dissolved in CH_2Cl_2 (50 mL) and the organic phase was dried over Na_2SO_4 before being concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2/ CH_2Cl_2:Hexanes: 60:40) The first fraction was 9 (158 mg, 0.154 mmol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.15 (s, 2H), 7.66 (s, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.23–7.15 (m, 10H), 7.06–6.98 (m, 4H), 6.88–6.85 (m, 8H), 4.79–4.78 (m, 4H), 2.62 (hep, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 2.5 Hz, 2H), 1.03 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$ 298 K): δ = 166.9, 163.3, 155.4, 155.3, 155.1, 154.3, 145.6, 135.4, 133.1, 130.9, 130.7, 129.9, 129.8, 129.6, 129.4, 128.8, 124.33, 124.31, 123.8, 122.2, 121.1, 121.0, 120.6, 119.8, 119.7, 118.4, 77.1, 75.5, 53.0, 29.0, 24.0. HR-ESI-MS: *m/z* Calcd: 1013.3200; found: 1013.3237. The second fraction was 8 (180 mg, 0.19 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.69 (s, 4H), 7.27–7.23 (m, 8H), 7.08 (t, *J* = 7.4 Hz, 4H), 6.91–6.88 (m, 8H), 4.85–4.83 (m, 8H), 2.46 (t, *J* = 2.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$ 298 K): δ = 167.2, 155.7, 153.7, 135.7, 131.1, 130.0, 129.0, 124.3, 121.5, 119.9, 118.9, 77.4, 75.6, 53.1. HR-ESI-MS: *m/z* Calcd: 948.2207; found: 948.2255.

Synthesis of LH-2: Compound 8 (16 mg, 0.017 mmol), 2 (32.5 mg, 0.13 mmol), $CuSO_4.5H_2O$ (4.2 mg, 0.017 mmol) and sodium ascorbate (3 mg, 0.015 mmol) were dissolved in a

mixture of solvents $CHCl_3$ (2 mL) / EtOH (1 mL) / H_2O (1 mL) in a microwave reaction vial and the reaction mixture was stirred under microwave irridation at 65 °C for 1 h. Then the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by thin layer chromatography (TLC) (MeOH:CH_2Cl_2 : 6%) to afford dendrimer LH-2 as a yellow solid (29 mg, 0.015 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.90 (s, 4H), 7.62 (s, 4H), 7.40–7.36 (m, 4H), 7.20–7.16 (m, 4H), 7.04–7.00 (m, 4H), 6.80 (d, *J* = 7.7 Hz, 8H), 6.76–6.73 (m, 8H), 6.07 (d, *J* = 1.1 Hz, 1H), 5.29 (s, 8H), 4.76 (t, *J* = 5.1 Hz, 8H), 4.40 (t, *J* = 5.1 Hz, 8H), 2.29 (d, *J* = 1.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 167.5, 160.9, 160.5, 155.5, 154.9, 153.3, 152.3, 142.5, 135.3, 129.7, 129.2, 125.7, 125.2, 124.0, 121.3, 119.4, 119.2, 118.5, 114.2, 112.4, 112.2, 101.7, 66.5, 58.7, 49.4, 18.6. HR-ESI-MS: *m/z* Calcd: 1928.5408; found: 1928.5458.

Synthesis of LH-3: Compound 9 (14 mg, 0.014 mmol), 2 (13 mg, 0.054 mmol), $CuSO_4.5H_2O$ (1.7 mg, 0.007 mmol) and sodium ascorbate (1.2 mg, 0.006 mmol) were dissolved in a mixture of solvents $CHCl_3$ (2 mL) / EtOH (1 mL) / H_2O (1 mL) in a microwave reaction vial and the reaction mixture was stirred under microwave irridation at 65 °C for 1 h. After the reaction was complete, the solvent was removed under reduced pressure and the residue was purified by thin layer chromatography (TLC) (MeOH:CH_2Cl_2 : 4%) to afford dendrimer LH-3 as a pink solid (20 mg, 0.013 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.12 (s, 2H), 7.85 (s, 2H), 7.63 (s, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.19–7.14 (m, 8H), 7.02–6.98 (m, 4H), 6.83 (d, *J* = 8.5 Hz, 8H), 6.73–6.71 (m, 4H), 6.05 (s, 2H), 5.25 (s, 4H), 4.71 (t, *J* = 5.0 Hz, 4H), 4.36 (t, *J* = 5.0 Hz, 4H), 2.60 (m, 2H), 2.28 (s, 6H), 1.03 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 167.5, 163.2, 160.9, 160.6, 155.4, 155.0, 154.2, 152.3, 145.6, 142.5, 135.4, 133.1, 130.7, 130.1, 129.9, 129.8, 129.3, 125.8, 125.2, 124.3, 124.26, 123.8, 122.2, 121.0, 120.6, 120.2, 119.7 (2C), 119.5, 118.4, 114.3, 112.5, 112.1, 101.8, 66.6, 58.8, 49.5, 29.7, 29.0, 24.0, 18.6. HR-ESI-MS: *m/z* Calcd for [M+H$^+$]: 1504.4801; found: 1504.4898.

Acknowledgements

The authors would like to thank to Ataturk University Research Fund for its support of this project (2011/375).

Notes and references

[a] Department of Chemistry, Ataturk University, Erzurum, 25240, Turkey. E-mail: oaltanbozdemir@atauni.edu.tr;

Electronic Supplementary Information (ESI) available: Experimental procedures, characterization of new compounds, and spectra. See DOI: 10.1039/c000000x/

References

1 (a) Z. Yuan, Y. Xiao, Z. Li and X. Qian, *Org. Lett*., 2009, **11**, 2808–2811; (b) Y. Xie, X. Zhang, Y. Xiao, Y. Zhang, F. Zhou, J. Qi and J. Qu, *Chem. Commun*., 2012, 4338–4340; (c) Y. Zhang, Z. Zhao, X. Huang, Y. Xie, C. Liu, J. Li, X. Guan, K. Zhang, C. Cheng and Y. Xiao, *RSC Adv*., 2012, **2**, 12644–12647.

2 (a) Z. Yuan, Y. Xiao and X. Qian, *Chem. Commun*., 2010, **46**, 2772–2774; (b) Y. Li, C. Wang, C. Li, S. Di Motta, F. Negri and Z. Wang, *Org. Lett*., 2014, **14**, 5278–5281.

3 (a) A. Arnaud, J. Belleney, F. Boue, L. Bouteiller, G. Carrot and V. Wintgens, *Angew. Chem. Int. Ed*., 2004, **43**, 1718–1721; (b) X. Mo, H.-Z. Chen, M-M. Shi and M. Wang, *Chem. Phys. Lett*., 2006, **417**, 457–460; (c) T. Martinsky, R. Hertmanowski, R. Stolarski and D. Bauman, *Thin Solid Films*., 2008, **516**, 8834–8838; (d) X. Mo, M.-M. Shi, J.-C. Huang, M. Wang and H.-Z. Chen, *Dyes Pigm*., 2008, **76**, 236–242.

4 Y. Zagranyarski, L. Chen, D. Jansch, T. Gessner, C. Li and K. Mullen, *Org. Lett.*, 2014, **16**, 2814–2817.

5 (a) X. Zhang, Y. Wu, J. Li, F. Li and M. Li, *Dyes Pigm*., 2008, **76**, 810–816; (b) C. Xue, R. Sun, R. Annab, D. Abadi and S. Jin, *Tet. Lett.*, 2009, **50**, 853–856; (c) J. Keiber, H. Bock, O. Thiebaut, E. Grelet and H. Langhals, *Eur. J. Org. Chem*., 2011, **4**, 707–712; (d) R. Wang, Z. Shi, C. Zhang, A. Zhang, J. Chen, W. Guo and Z. Sun, *Dyes Pigm*., 2013, **98**, 450–458.

6 (a) N. S. Lewis, *Nature* 2001, **414**, 589–590; (b) Y. Nakamura, N. Aratani and A. Osuka, *Chem. Soc. Rev*., 2007, **36**, 831–845; (c) M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910–1921; (d) M. J. Currie, J. K. Mapel, T. D. Heidel, S. Goffri and M. A. Baldo, *Science*, 2008, **321**, 226–228; (e) R. Ziessel and A. Harriman, *Chem. Commun*., 2011, **47**, 611–631; (f) D. Hablot, A. Harriman and R. Ziessel, *Angew. Chem. Int. Ed*., 2011, **50**, 7833–7836; (g) D. G. Nocera, *Acc. Chem. Res*., 2012, **45**, 767–776; (h) S. Berardi, S. Drouet, L. Francas, C. Gimbert-Surinach, M. Guttentag, C. Richmond, T. Stoll and A. Liobet, *Chem. Soc. Rev*., 2014, DOI: 10.1039/c3cs60405e.

7 (a) H. Imahori, *J. Phys. Chem. B*., 2004, **108**, 6130–6143; (b) W-S. Li and T. Aida, *Chem. Rev*., 2009, **109**, 6047–6076; (c) Y. Zeng, Y.-L. Li, J. Chen, G. Yang and Y. Li, *Chem. Asian J*., 2010, **5**, 992–1005; (d) M. Kozaki, S. Morita, S. Suzuki and K. J. Okada, *J. Org. Chem*., 2012, **77**, 9447–9457; (e) R. Ziessel, G. Ulrich, A. Haefele and A. Harriman, *J. Am. Chem. Soc*., 2013, **135**, 11330–11344; (f) M. Kozaki, S. Suzuki and Okada, K. *Chem. Lett*. 2013, 42, 1112–1118.

8 (a) J. M. Serin, D. W. Brousmiche and J. M. J. Frechet, *Chem. Commun*., 2002, 2605–2607; (b) M. Cotlet, T. Vosch, S. Habuchi, T. Weil, K. Mullen, J. Hofkens and F. De Schryver, *J. Am. Chem. Soc*., 2005, **127**, 9760–9768; (c) J. H. Hurenkamp, W. R. Browne, R. Augilis, A. Pugzlys, P. H. M. van Lousdrecht, J. H. van Esch and B. L. Feringa, *Org. Biomol. Chem.*, 2007, **5**, 3354–3362; (d) O. A. Bozdemir, M. D. Yilmaz, O. Buyukcakir, A. Siemiarczuk, M. Tutas and E. U.Akkaya, *New J. Chem*., 2010, **34**, 151–155; (e) T. Weil, T. Vosch, J. Hofkens, K. Peneva and K. Mullen, *Angew. Chem. Int. Ed*., 2010, **49**, 9068–9093; (f) H. Langhals, A. J. Esterbauer, A. Walter, E. Riedle and I. Pugliesi, *J. Am. Chem. Soc*., 2010, **132**, 16777–16782; (g) M. Takahashi, H. Morimoto, K. Miyake, H. Kawaki, Y. Sei, K. Yamaguchi, T. Sengoku and H. Yoda, *New J. Chem.*, 2008, **32**, 547–553.

9 (a) P. Apukuttan, W. Dehaen, V. V. Fokin and E. Van der Eycken, *Org. Lett*., 2004, **6**, 4223–4225; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2002, **41**, 2596–2599; (c) M. Meldal and C. W. Tornoe, *Chem. Rev*., 2008, **108**, 2952–3015.

10 (a) Y. Nagao, T. Naito, Y. Abe and T. Misono, *Dyes Pigm*., 1996, **32**, 71–83.

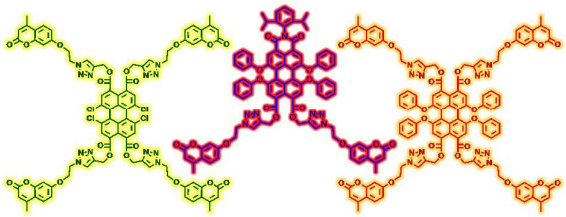
11 D. Su, J. Oh, S.-C. Lee, J. M. Lim, S. Sahu, X. Yu, D. Kim and Y.-T. Chang, *Chem. Sci*. 2014, DOI: 10.1039/C4SC01821D.

12 (a) D. V. Roberts, B. P. Wittmershaus, Y.-Z. Zhang, S. Swan and M. P. J. Klinosky, *J. Lumin*. 1998, **79**, 225–231; (b) Z. Kostereli, T. Ozdemir, O. Buyukcakir and E. U. Akkaya, *Org. Lett*., 2012, **14**, 3636–3639; (c) S. Guo, L. Ma, J. Zhao, B. Kucukoz, A. Karatay, M. Hayvali, H. G. Yaglioglu and A. Elmali, *Chem. Sci.*, 2014, **5**, 489–500.

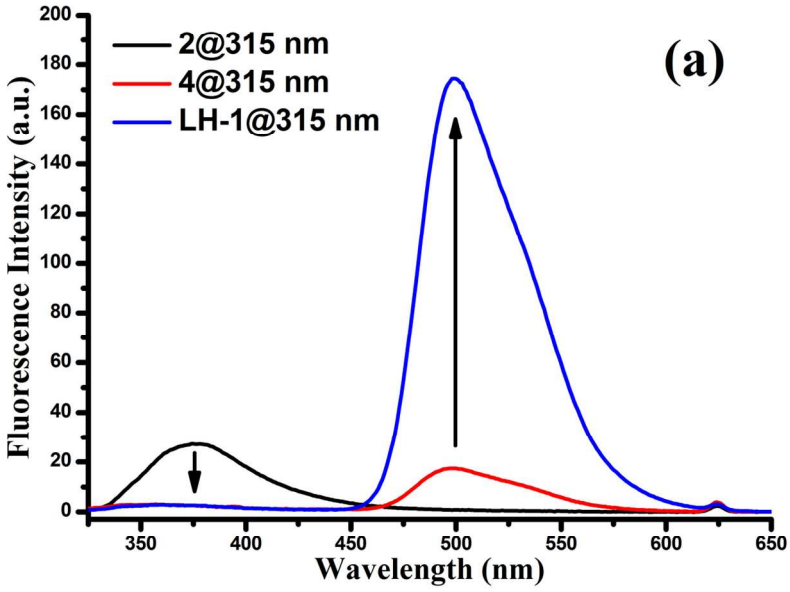
13 Y.-C. Duan, Y.-C. Ma, E. Zhang, X.-J. Shi, M.-M. Wang, X.-W. Ye and H.-M Liu, *Eur. J. Med. Chem.* 2013, **62**, 11–19.

14 R. S. Sanchez, R. Gras-Charles, J. L. Bourdelande, G. Guirado and J. Hernando, *J. Phys. Chem C.* 2012, **116**, 7164–7172.

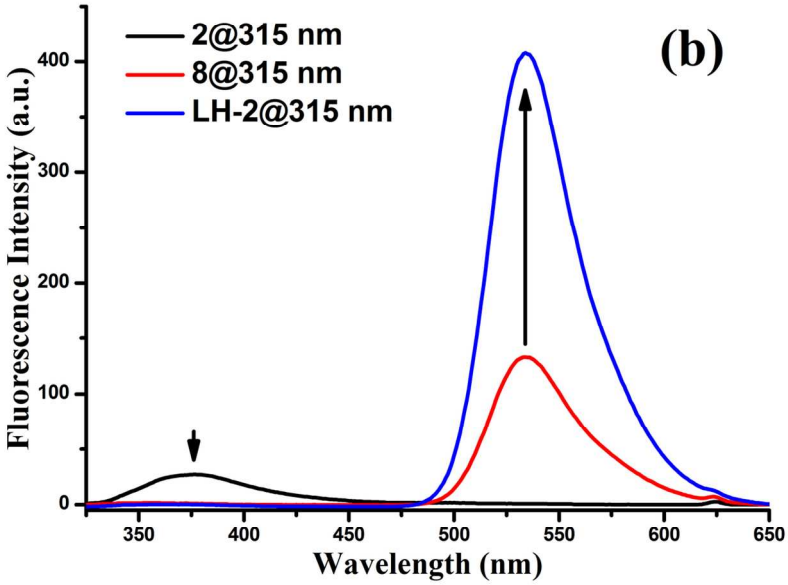
15 *Principals of Fluorescence Spectroscopy*, J. R. Lakowicz, Springer, Singapore, 2006.



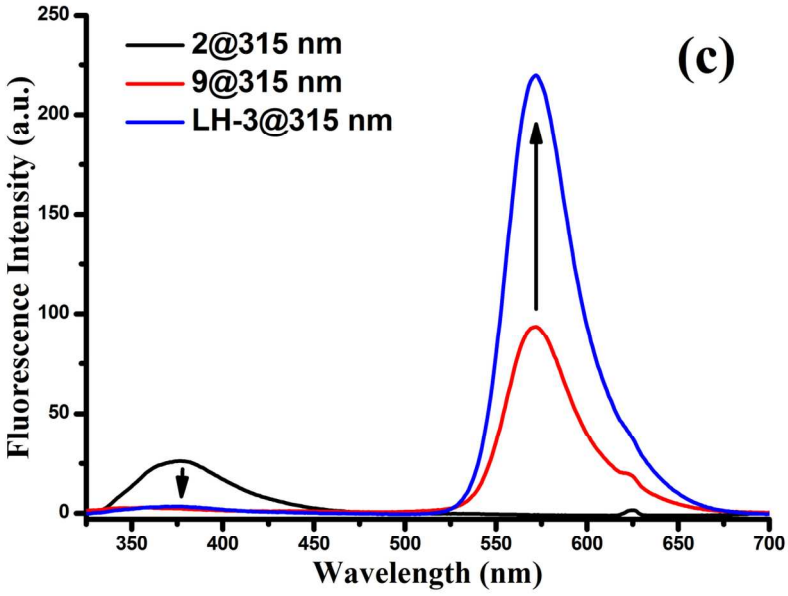
Novel perylene derivatives are ready to be used as functional energy acceptors in light-harvesting systems.



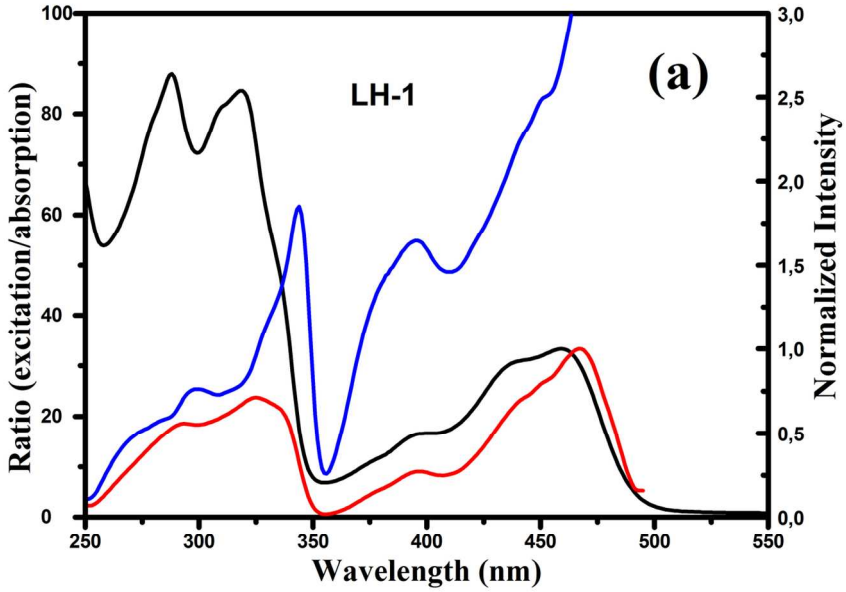
134x94mm (300 x 300 DPI)



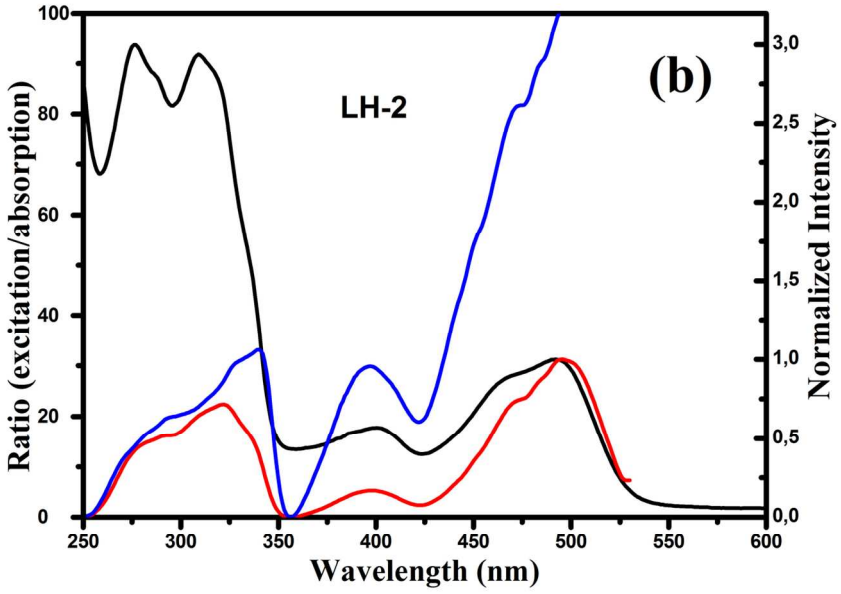
134x94mm (300 x 300 DPI)



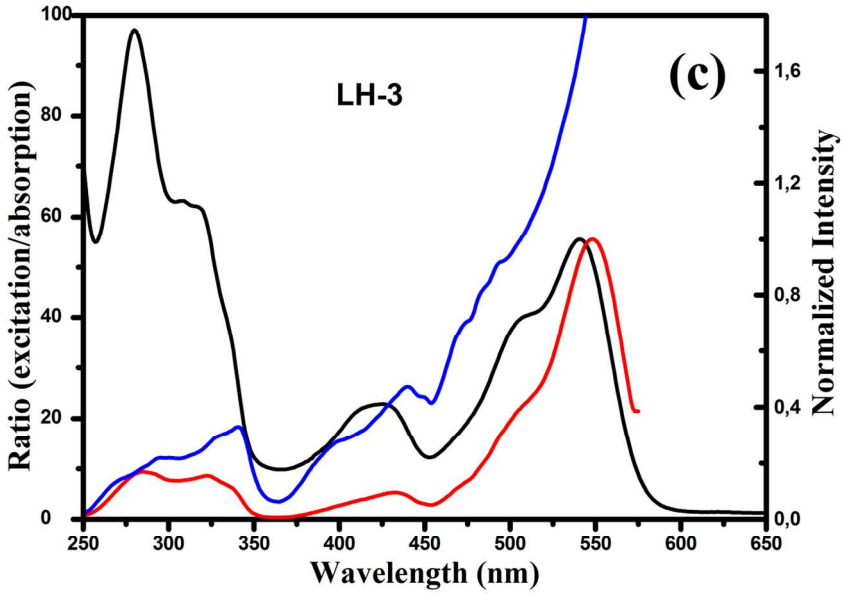
134x94mm (300 x 300 DPI)



134x94mm (300 x 300 DPI)



134x94mm (300 x 300 DPI)



134x94mm (300 x 300 DPI)