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Pyrene-Excimers-Based Antenna Systems

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Abstract: A series of dendrimeric compounds bearing pyrene units were synthesized to afford light-harvesting antennae based on the formation of intramolecular excimers. The synthetic plan profited from the efficiency of the Huisgen reaction, the 1,3-dipolar cycloaddition of azides and terminal alkynes, which allowed ready assembly of the different building blocks. The three molecular antennae obtained, of increasing generation, revealed efficient energy transfer both in solution and in the solid state.

Keywords: azides · catalysis · cycloaddition · dendrimers · energy transfer

Introduction

Among the fluorescent chromophores used for the production of devices, pyrene draws the highest attention. Such wide interest is due to the peculiar properties of this molecule, which can form excimers[1] even at relatively low concentration. The photophysical properties of pyrene excimers have been, in fact, studied over quite a few years.[2] The grafting of more than a pyrene unit on a suitable scaffold makes the formation of the excimers concentration independent.[3] The new fluorescent properties of the excimeric species are at the basis of analytical applications[4] because of the strong dependence of fluorescence on the environment.[5] The high sensitivity of fluorescence detection makes such an approach very fruitful.[6] Much less addressed by investigators has been the possibility of decorating the periphery of the dendrimers with pyrene units. Nevertheless, a dendrimer might be an excellent scaffold to anchor many chromophores together and give rise to the formation of a number of intramolecular excimers. This possibility was rather used as a probe to study the structural characteristics of dendrimers than for the production of devices.[7,8,9]

As a result of our ongoing research into the synthesis of light-harvesting antennae,[10,11] we were interested in the synthesis of new dendrimers with their outer parts decorated with pyrene units to build up light-harvesting systems based on the excimeric fluorescence of pyrene, thus profiting from the supramolecular process (i.e., the excimer formation) within a molecular assembly. Such an approach has, to the best of our knowledge, only one precedent concerning the quenching of the pyrene excimers through a FRET process.[12] Furthermore, the possibility of inducing electroluminescence makes it possible to anticipate applications in the field of organic light-emitting devices (OLEDs).[13] For a simple and efficient build up of the saturated scaffold, the Huisgen reaction was chosen as, after the recent development of the catalytic form,[14] it has been demonstrated to be a reliable and efficient synthetic tool.[15,16] Using a simple variation of a procedure described by Fokin and co-workers,[15] which proved to be efficient for the construction of complex dendrimeric structures, the preparation of three

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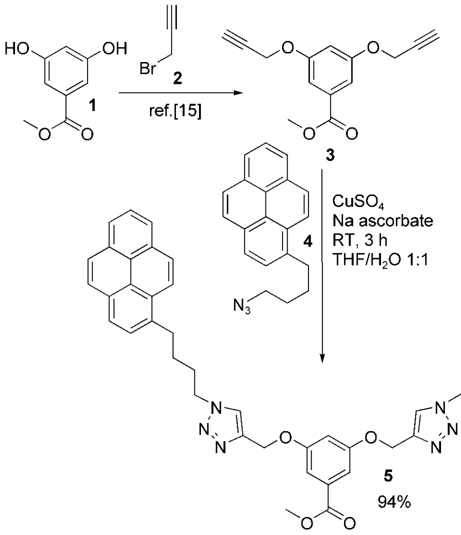
dendrimeric compounds substituted with pyrene units at the periphery was successfully carried out.

Results and Discussion

The first generation of the pyrene-substituted dendron was readily obtained starting from ester **1**,[15] which was converted into the diacetylenic compound **3**.[15] The Cu^I-catalyzed Huisgen reaction afforded finally **5** (Scheme 1). The relatively long arm that characterizes the pyrene units was chosen to guarantee full flexibility in the final assembly and to avoid any steric obstacle in the formation of the excimeric species. The reaction was very efficient and afforded **5** in high yield.



Scheme 1. Cu^I-catalyzed Huisgen reaction to yield compound **5**.

The structure of **5** was readily assigned on the basis of its very symmetrical ^{1}H NMR spectrum, the signal at $\delta = 7.43$ ppm (s, 2H) was assigned to the protons on the triazole rings (see the Experimental Section). The spectroscopic properties of this first model compound were investigated in several different deoxygenated solvents. The absorption and emission data are summarized in Table 1.

The UV absorption spectra were characterized by two well-structured bands at roughly 275 and 345 nm, typical of the pyrene units, whereas the emission spectra exhibited typical monomeric pyrene fluorescence and a broad, featureless emission centered at approximately 475 nm. The last overriding contribution was observed even at very low concentration (10^{-6} M); therefore, the signal can be attributed to intramolecular excimer formation. Although the UV absorption was not significantly sensitive to the nature of the solvent, the photoluminescence spectra varied markedly with that. It is well known that in bis(pyrenil) compounds the extent of excimer emission was limited by the probability of a molecule reaching, within the lifetime of the excited state, a conformation suitable for excimer formation and by the stabilization of the excimer.[17] The observed ratio between the excimer and monomeric fluorescence quantum yield $\Phi_F^{EXC}/\Phi_F^{MON}$ was plotted in Figure 1 as a function of the viscosity of the solvent. Despite the different molecular nature, the ratio decreased sharply as the η value increased[18] and became zero at high viscosity.

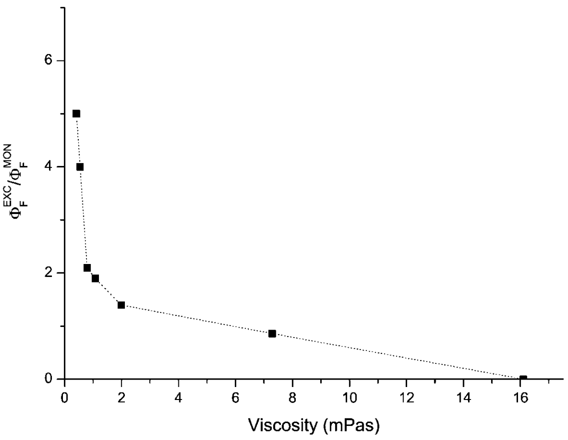


Figure 1. Plot of the $\Phi_F^{EXC}/\Phi_F^{MON}$ variation with the viscosity η of the solvent. The line is just a guide for the eye.

Table 1. The wavelengths of maximum absorption λ^{MAX}, emission wavelengths λ^{EM}, and fluorescence quantum yields Φ_F for **5**.[a]

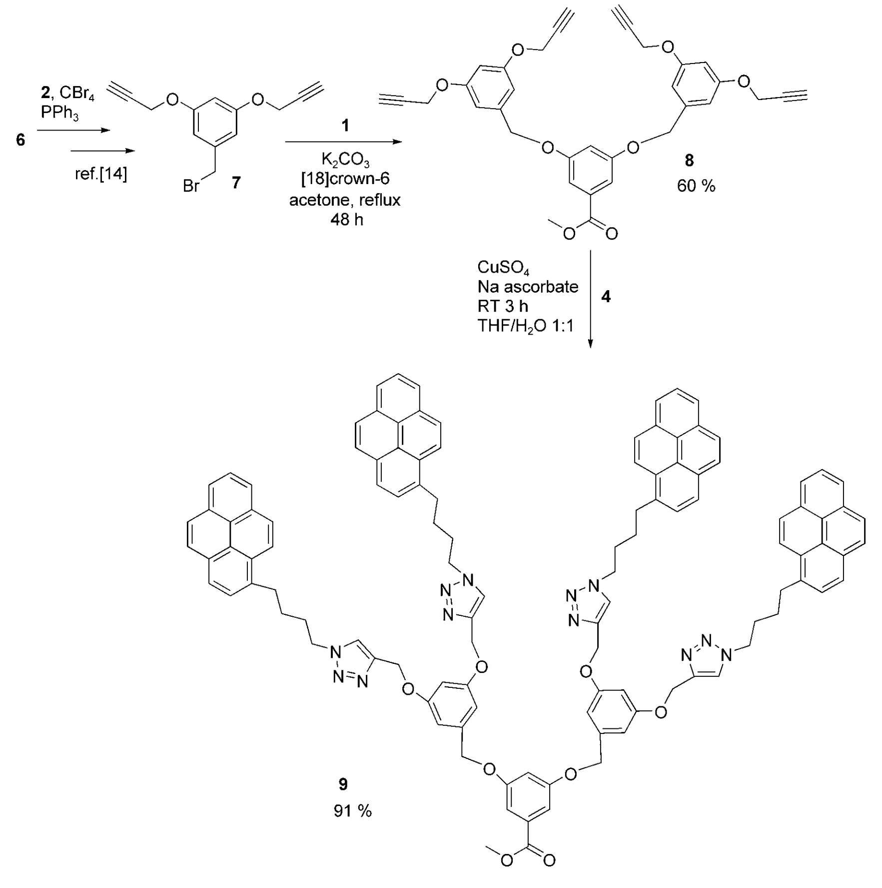
Solvent	λ_1^{MAX} [nm]	λ_2^{MAX} [nm]	λ^{EM} [nm]	Φ_F^{MON}	Φ_F^{EXC}	$\Phi_F^{EXC}/\Phi_F^{MON}$
dichloromethane	277	344	377/397	0.028		5.0
			475		0.14	
methanol	275	342	377/396	0.025		4.0
			477		0.10	
DMF	277	345	377/397	0.08		2.1
			475		0.17	
ethanol	275	342	376/397	0.05		1.8
			476		0.09	
dimethyl sulfoxide	278	346	378/398	0.11		1.4
			481		0.16	
1-octanol	277	344	377/397	0.13		0.85
			476		0.11	
ethylene glycol	277	344	377/397	0.23	0	0

[a] The λ^{MAX}, λ^{EM}, and Φ_F values were collected in solutions (10^{-6} M); MON and EXC indicate the monomeric pyrene and the intramolecular excimer fluorescence, respectively; the excitation wavelength was 275 nm in CH_2Cl_2 and 345 nm in the other solvents.

Encouraged by the interesting properties of the first generation dendron, the synthesis of the two subsequent generations of the donor scaffold, that is, compounds **9** and **13**, was also undertaken and achieved by following the same approach, with small variations, in excellent yield (Scheme 2 and Scheme 3). The branching units **6** and **7** were used to increase the number of acetylenic groups at the periphery.

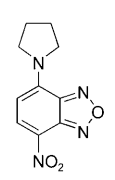
The UV absorption and fluorescence spectra of **5**, **9**, and **13** were recorded in DMF (Figure 2). The study was restricted to DMF as the solvent because of the limited solubility of **9** and **13** in other solvents. The UV absorption spectra that resulted are almost superimposable for the three different compounds. In contrast, in the fluorescence spectra, the ratio of excimer/monomer emission was dependent on the generation of the three compounds, with the maximum emission observed for **13**.

For the production of light-harvesting antenna systems, a suitable acceptor chromophore that has to fulfill the main requisite of the Förster theory,[19] which is generally applied for non-conjugated light-harvesting antenna systems, was needed. The requisite was that the fluorescence spectra of the donor chromophore should overlap with the absorption spectrum of the acceptor one. For this reason, a fluorophore with a maximum absorption at around 500 nm should be linked to the dendrimer. Two suitable candidates, **14** and **15**, were accordingly identified.



Scheme 2. Synthesis of dendron **9**.

Nitrobenzofurazane **14** is a suitable fluorophore that was previously used by us in other antenna systems.[11] Commercially available as a chloride salt, **14** becomes fluorescent after conjugation with an amino group. Styrylpyridinium derivatives, such as **15**, which are readily available from the alkylation of the pyridine nitrogen atom of *N*,*N*-diethyl-*N*-[4-{(*E*)-2-(4-pyridinyl)ethenyl}phenyl]amine (**19**),[20,21] are versatile fluorophores that are well-known red emitters used mainly as fluorescent probes. In both cases, the absorption of the potential acceptor chromophores overlaps efficiently with the excimeric emission of the donor (see Figure 1 in the Supporting Information). Compounds **14** and **15** appear to be suited for the construction of a light-harvesting system in which **5** will act as the donor in an intramolecular energy-transfer process.



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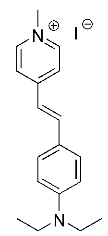
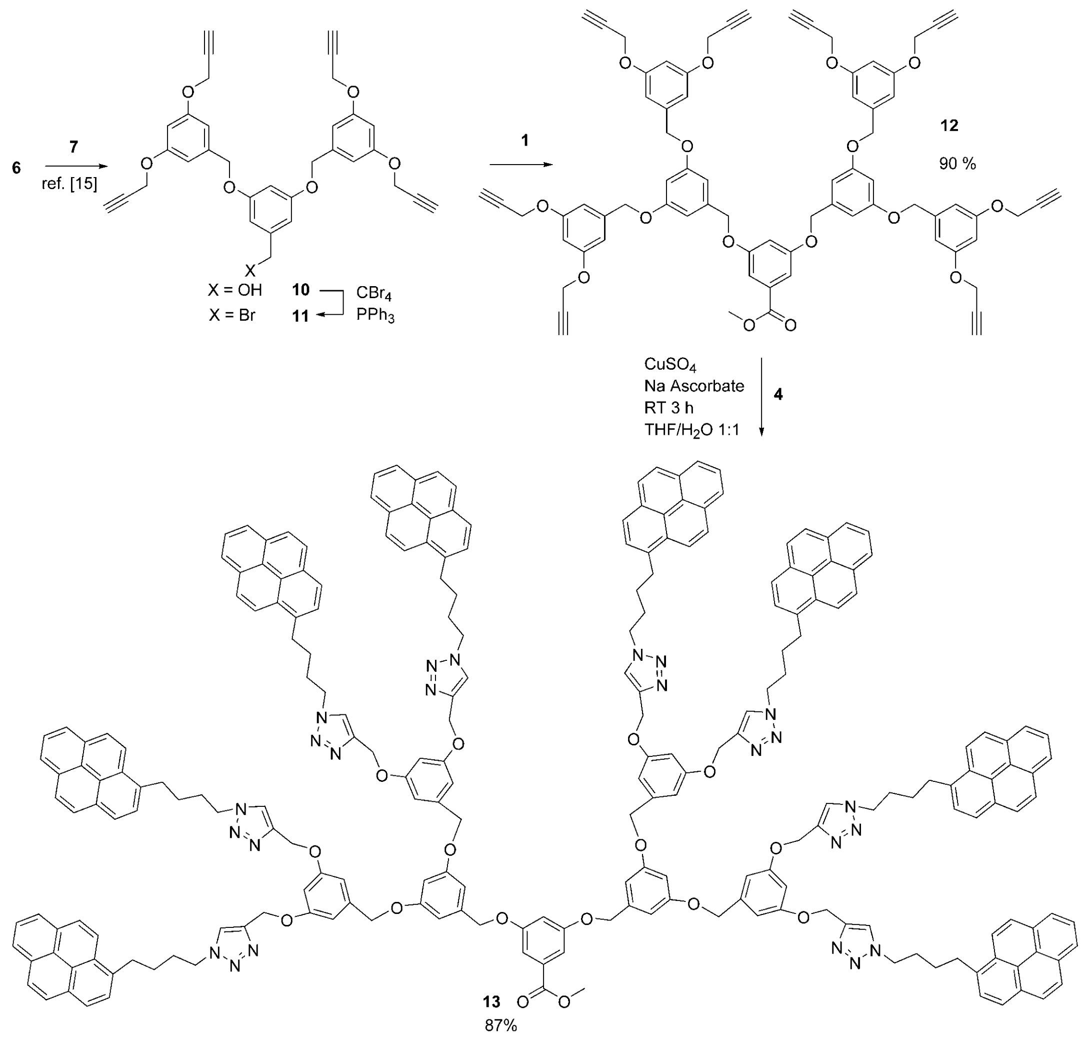


15

For the synthesis of the antenna system, it was necessary to modify the structure of the dendron to anchor the acceptor chromophore to the structure. To this end, dendron **16** was synthesized. Substitution of the terminal bromine atom with a secondary amine and the final S_NAr process with chloride **17** afforded **18**, a simple model of an antenna (overall yield: 92 %). The same intermediate **16** was treated with 4-styryl-pyridine derivative **19** to afford pyridinium salt **20** in 76 % yield (Scheme 4).

The absorption spectra of **18** and **20** were compared to the absorption spectra of the isolated donor and acceptor chromophores (Figure 3). The donor and acceptor portions could interact appreciably in the antenna systems **18** and **20**, in fact the bands associated with the acceptor underwent an ipochromism. The effect was strongly apparent in the UV spectrum of **18**, in which the molar extinction coefficient showed a 30 % decrease (Figure 3). On the other hand, a red shift was evident only in the UV spectrum of **20**. These data suggested that the optical properties of the acceptor moiety in the antenna system could not be considered as an equivalent of the chromophore in solution.

Compound **18**, the first to be analyzed, showed some disap-



Scheme 3. Synthesis of dendron **13**.

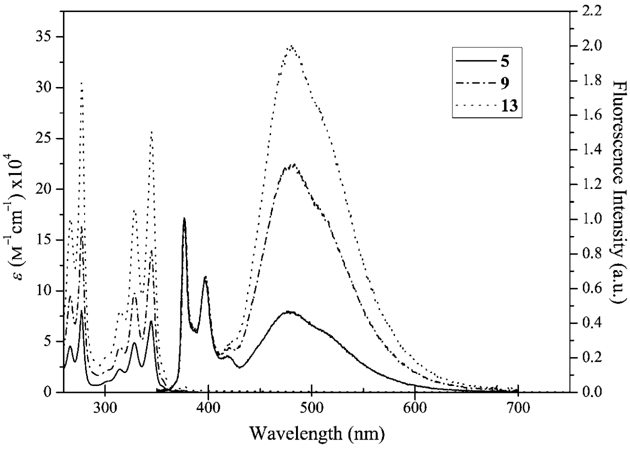
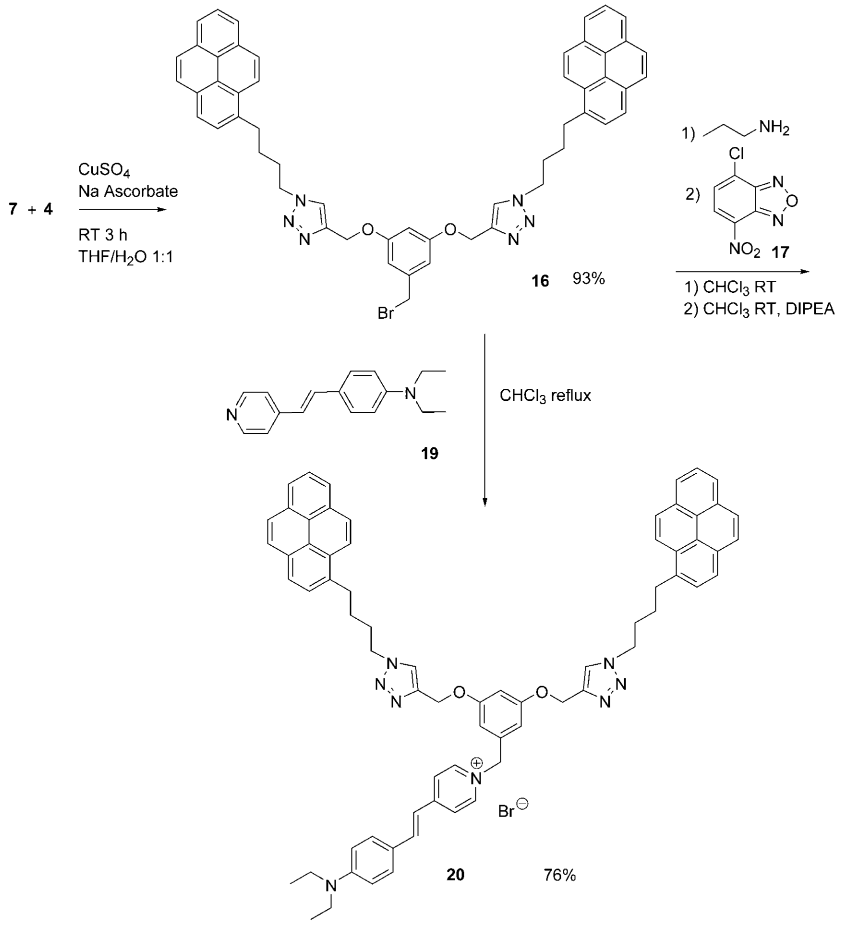


Figure 2. UV absorption and fluorescence ($\lambda_{exc}=345$ nm) spectra of **5**, **9**, and **13** in DMF. The emission profiles were normalized at 377 nm.

pointing features that suggested that the study should be stopped. In fact, because of a blue shift of more than 10 nm (data not showed) of the acceptor emission, the resulting spectrum showed a very poorly resolved band caused by the overlapping of the excimeric emission with the emission of the acceptor. Much more rewarding results were obtained with **20**, whose emission spectrum (i.e., $\lambda_{ecx}=345$ nm) is reported in Figure 4. The fluorescence emission was normalized at 377 nm, which corresponds to the value of maximum intensity, and we emphasized the fact that we obtained the emission in the whole visible spectrum. To prevent misleading information from the figure, we noticed that the fluorescence quantum yield (see Table 2) both of the monomer and of the excimer decreased going from donor to antenna molecule.

The concentration was kept very low (3.5×10^{-7} M) to avoid any intermolecular effects. In the emission profile, it was easy to recognize three different contributions from the monomeric pyrene, the excimer emission and the acceptor emission. The hypothesis of a direct excitation of the last chromophore was excluded by the absence of an emission from a solution of **15** excited at the same wavelength and concentration reported above. This evidence guaranteed the intramolecular nature of the process.



Scheme 4. Synthesis of compound **18** and pyridinium salt **20**. DIPEA = diisopropylethylamine.

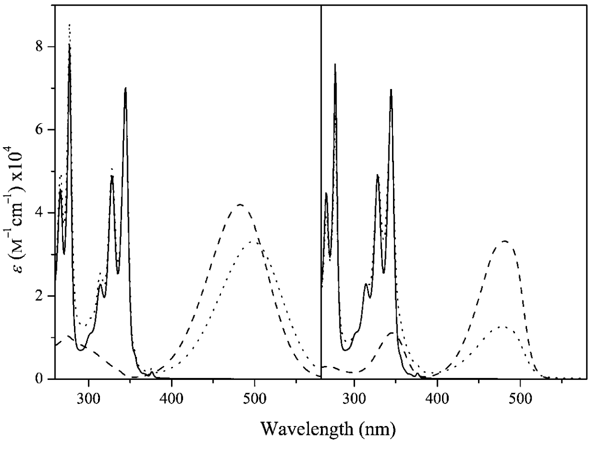


Figure 3. The absorption spectra (dotted line) of **18** (right) in CH_2Cl_2 and **20** (left) in DMF were compared to their correspondent donor (solid line) and acceptor (dashed line) moieties.

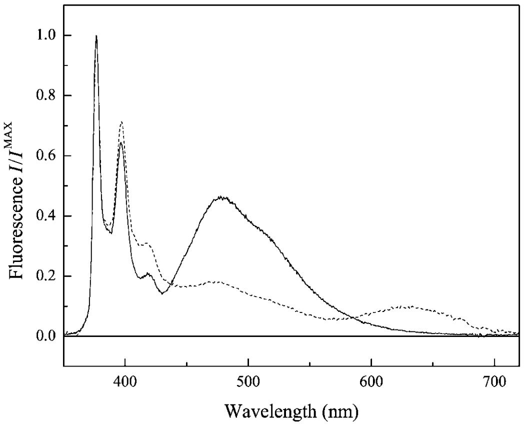


Figure 4. Normalized emission spectra of **20** (dashed line) and **5** (continuous line) in DMF.

The total (monomer + excimer) fluorescence quantum yield (Φ_{FD}) of the donor in the antenna system (i.e., **20**) was compared with that of the dendron (i.e., **5**) $(\Phi_{FD})_0$, both excited at 345 nm. For a simple donor/acceptor system, it is possible to estimate the quantum efficiency f of the energy transfer by the ratio reported in Equation (1).[22]

$$\frac{\Phi_{FD}}{(\Phi_{FD})_0} = 1-f \tag{1}$$

From the data reported in Table 2, a value of $f = 0.9$ was cal-

Table 2. Emission data of **5**, **9**, **13**, **20**, **21**, and **23**.[a]

		Dendrons			Antennae		
Entry		**5**	**9**	**13**	**20**	**21**	**23**
1	Φ_F^{MON}	0.08 ± 0.01	0.029 ± 0.004	0.031 ± 0.005	0.014 ± 0.002	0.0053 ± 0.0007	0.007 ± 0.001
2	Φ_F^{EXC}	0.17 ± 0.04	0.20 ± 0.03	0.32 ± 0.06	0.016 ± 0.003	0.013 ± 0.002	0.0048 ± 0.0009
3	$(\Phi_{FA})_D$ ($\lambda = 345$ nm)	–	–	–	0.006 ± 0.002	0.009 ± 0.002	0.018 ± 0.002
4	q_{FA} ($\lambda = 488$ nm)	–	–	–	0.007 ± 0.001	0.011 ± 0.002	0.018 ± 0.002
5	$\Phi_F^{EXC}/\Phi_F^{MON}$	2.1	6.9	10.3	1.1	2.4	0.7
6	f[b]	–	–	–	0.5	0.65	0.93

[a] The fluorescence quantum yield of the monomer and of the excimer are given in entries 1 and 2, respectively; the fluorescence quantum yields of the acceptor in the antenna system indirectly excited at 345 nm and directly excited by absorption at 488 nm and are given in entries 3 and 4. [b] f is the estimated energy-transfer efficiency.

culated. However, such a high value surely overrated the real efficiency because, in this case, the energy transfer was complicated by the presence of another process, that is, the excimer formation. Regardless of how complex the involved photophysical processes are, it is evident that the fluorescence quantum yield of the donor is decreased in the presence of the acceptor. The present study is limited to static measurements and does not allow full unveiling of the mechanism of the excimer pathway. Time-resolved measurements will be necessary to detail the process. Nevertheless, from the kinetic pathway shown in Figure 5, it was possible to determinate the relative quantum yield for the monomer and the excimer emission.

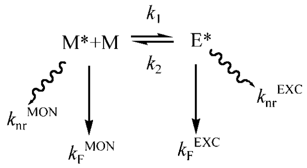


Figure 5. Schematic processes for excimer formation/deactivation. E = excimer, M = monomer, k_{nr} = non-radiative rate constant.

It is well known[23] that the accepted expression of a quantum yield emission is given by Equation (2):

$$\Phi_F = \Phi^* \frac{k_F}{\sum k_i} \tag{2}$$

where Φ^* is the formation efficiency of the emitting state, k_F is the rate constant of the emission, and Σk_i is the sum of all the rates involved in depopulation of the emission state. By defining R_0 and R, the ratios between the fluorescence quantum yields of the excimer and monomer relative to the dendron molecule and the antenna system, respectively, it was possible to demonstrate (see note i in the Supporting Information) that the ratio R/R_0 was strictly connected to the efficiency f of the energy-transfer process given in Equation (3).

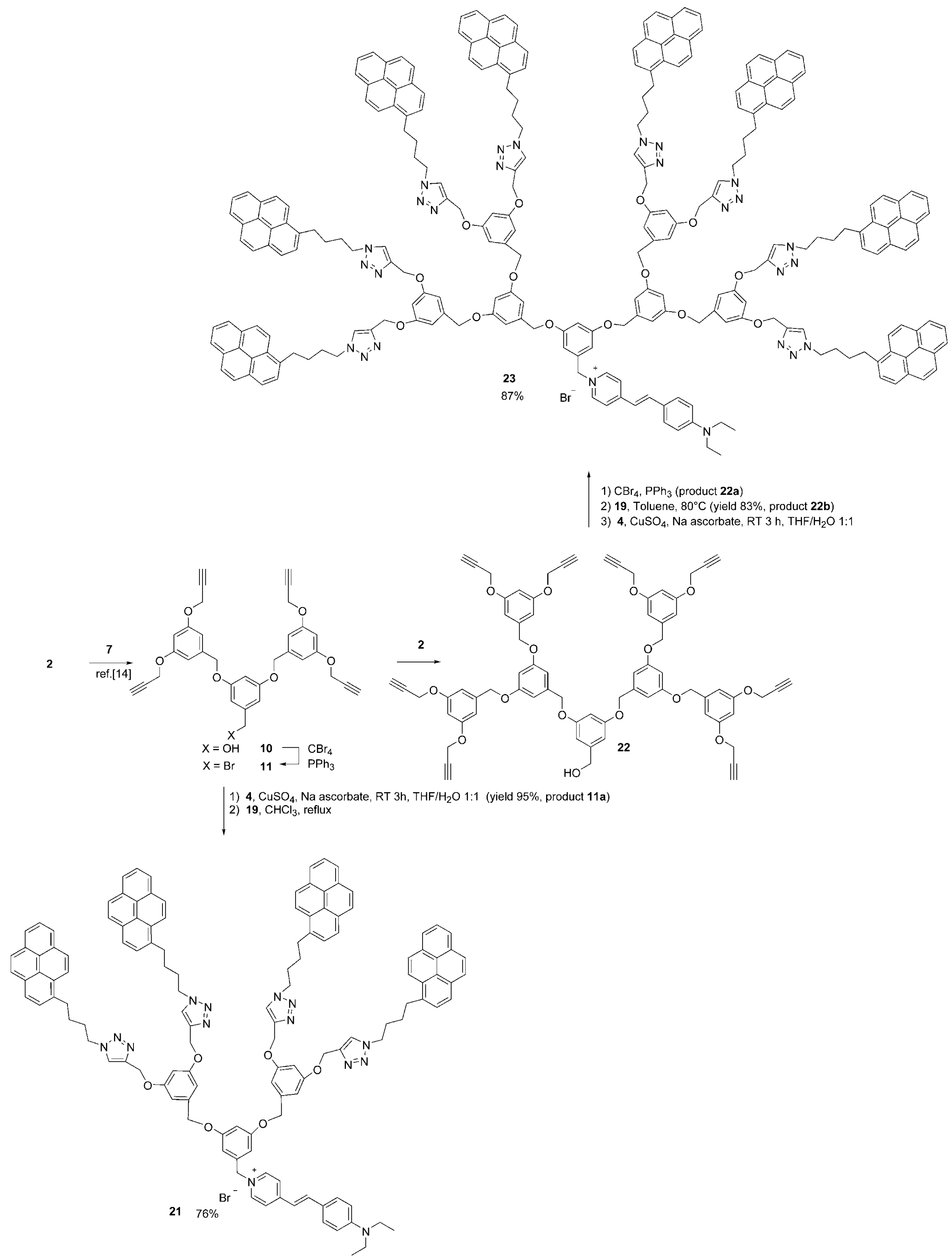
$$f = 1 - \frac{R}{R_0} \tag{3}$$

By applying Equation (3) to the data collected for **5** and **20** (Table 2, entry 5), the energy-transfer efficiency was 0.5.

On the basis of the results obtained with the first-generation compounds, the second- and third-generation compounds **21** and **23**, respectively, were synthesized. The synthesis was again performed by modifying the precedent synthesis of the donor dendrons (Scheme 5). In the last step of the synthesis of **21**, the alkylation of pyridine **19**, some evidence of decomposition was noticed, probably caused by prolonged heating in $CHCl_3$. For this reason, the 1,3-dipolar cycloaddition reaction, which took place at room temperature and overnight, was carried out as the final step in the synthesis of **23**. The purification of these molecular antennae was performed by chromatography on alumina, and all the compounds where fully identified and characterized by ESI mass-spectrometric, ^1H and ^{13}C NMR spectroscopic, and elemental analysis. The absorption and fluorescence spectra of **21** and **23** are reported in the Figure 6. The calculated fluorescence quantum yields Φ_F of the monomer and excimer and the efficiency of the dendrons and antennae are reported in Table 2.

The complete picture of the three antenna systems and their dendrons allowed an estimation of the energy-transfer efficiency, and a net increment passing from **20** to **23** was obtained. For a wider characterization of the spectroscopic properties of these compounds and to explore the potential application in OLEDs, their UV absorption and fluorescence spectra were obtained in the solid state. The three donors **5**, **9**, and **13** were studied as cast-films formed from diluted solutions in CH_2Cl_2.

The absorption spectra of the films (Figure 7) are slightly broadened and red shifted (5 nm) with respect to those of the solutions (see Figure 2). These results are in agreement with those reported for pyrene-based materials in the presence of pyrene preassociation[25] in the ground state. On the contrary, the emission spectra (Figure 7) exclusively showed the emission of the excimer. The different behavior observed in the solid state and in solution can be explained by the different nature of the excitations. In solution, excimer formation, at the low concentrations used, is an intramolecular process and dynamic excimers are formed after excitation thanks to the mobility of the pyrene units (influenced by the viscosity of the solvent). On the other hand, in the solid films, the tendency of the aromatic units toward π stacking induces partial pyrene aggregation or preassociation in the ground state and pyrene excimer formation occurs both intra- and intermolecularly. Because of the rigidity of the environment, static excimers are responsible



Scheme 5. Synthesis of the second- and third-generation compounds **21** and **23**.

for the emission in contrast to the dynamic excimers typical of the solutions.[2] The small red shift in the energy levels of the aggregated pyrenes observed in the films however makes them efficient energy traps for the excitation, which because of the fast intermolecular migration (Förster and Dexter energy transfers) typical of solid-state samples[25] re-

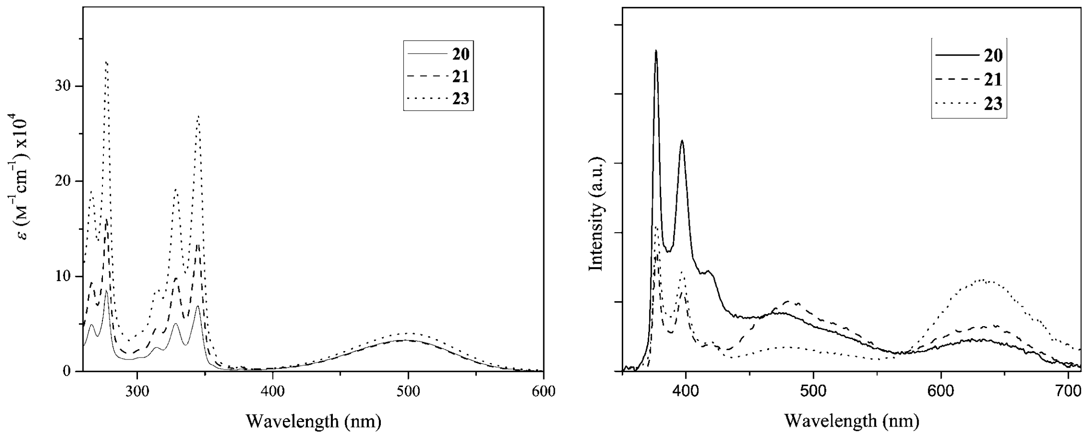


Figure 6. Absorption spectra (left) and fluorescence spectra (right) of **20**–**23**. The intensity of the emission profile was divided to the absorbance of the sample at $\lambda_{exc}=345$ nm.

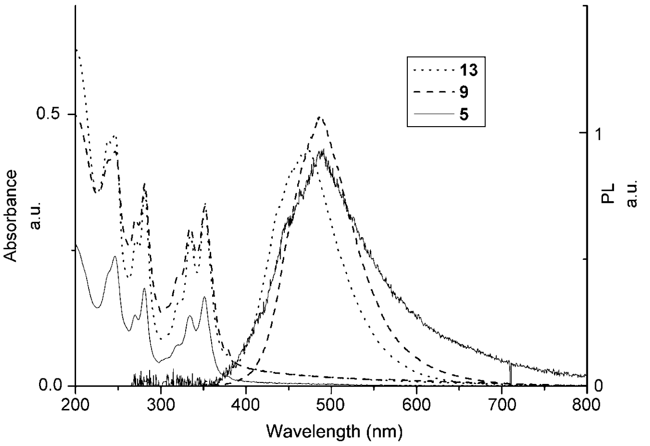


Figure 7. Solid-state (cast-film) absorption and fluorescence spectra of **5**, **9**, and **13**.

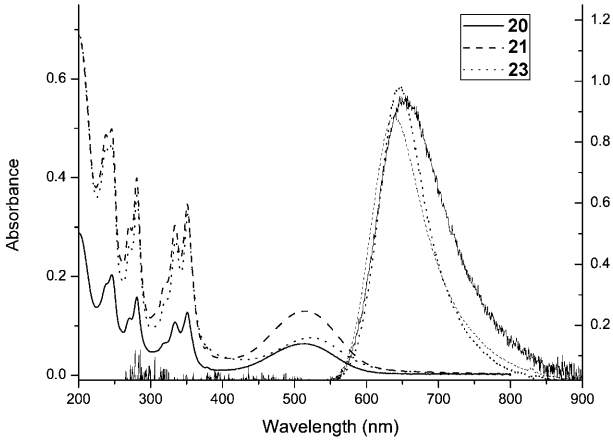


Figure 8. Absorption and emission spectra (cast-film) of **20**–**23**.

combine only from static excimers. The same measurements made with the isolated acceptor **15** showed that this molecule is almost non-fluorescent in the solid state ($\Phi_F < 0.01$ at $\lambda = 500$ nm), even if its fluorescence spectrum is not appreciably different from the spectrum obtained in solution (see Figure 2 in the Supporting Information).

This situation was radically altered in the molecular antennae. Again the absorption spectra did not show any remarkable variation (Figure 8), as it was the sum of the absorption spectra of the two chromophores, whereas the emission spectra showed exclusively the band associated with the emission of the acceptor (Figure 8, $\lambda = 350$ nm). The higher efficiency of the energy transfer in the solid state, with respect to the solution, might be because of the presence of both long-range Förster-type and short-range Dexter-type energy transfers.[25] All the data collected in the solid state are reported in Table 3.

The efficiency of the acceptor emission increases with the generation and reaches a very promising value of 0.13 for the third-generation antenna in the solid state. These results show that **21** and **23** can be used as red emitters in OLED applications.

Table 3. Fluorescence quantum yields of **5**, **9**, **13**, **15**, **20**, **21**, and **23** (cast-films).

Compound	$(\Phi_{FA})_D$ $\lambda = 350$ nm)	q_{FA} (λ=500 nm)
5	0.31	–
9	0.24	–
13	0.48	–
15	<0.01	<0.01
20	0.04	0.02
21	0.08	0.07
23	0.13	0.11

Conclusion

The synthesis of the third-generation compounds **20**, **21**, and **23** demonstrated the possibility of assembling molecular antenna systems based on the formation of excimers. The static spectroscopic study, although not able to give precise details of the complete energy-transfer process, suggests a high efficiency for all the systems assembled. From the analysis of the photoluminescence in the solid state, we have shown that because of energy-transfer and hopping processes, a pure red emission is attained. The quite high efficiency of this emission for the antenna systems of the second and third generation demonstrates that they are very promising red emitters for OLED applications.[26]

Experimental Section

Safety warning: Azides are potentially explosive. Maximum caution must be used when manipulating these compounds, especially in large-scale reactions.

Methyl 3,5-bis{[3,5-bis(2-propynyloxy)benzyl]oxy}benzoate (Acet$_4$-G2-COOCH$_3$) (8): A suspension of methyl 3,5-dihidroxybenzoate (**1**; 0.228 g, 0.93 mmol), 1-bromomethyl-3,5-bis(prop-2-ynyloxy)benzene (**7**; 0.530 g, 1.86 mmol, 2 equiv), K_2CO_3 (1.03 g, 7.46 mmol), and [18]crown-6 (5 mg) in acetone (25 mL) was heated to reflux under nitrogen for 48 h. The reaction mixture was then evaporated to dryness and partitioned between water and dichloromethane. The organic layer was dried over Na_2SO_4, evaporated, and the solid crystallized in methanol to give the product as white crystals (0.39 g, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=7.27$ (d, J(H,H) = 2.3 Hz, 2H), 6.26 (t, J(H,H) = 2.3 Hz, 1H), 6.68 (t, J(H,H) = 2.3 Hz, 4H), 6.57 (t, J(H,H) = 2.3 Hz, 2H), 5.02 (s, 4H), 4.68 (d, J(H,H) = 2.4 Hz, 8H), 3.90 (s, 3H), 2.52 ppm (t, J(H,H) = 2.4 Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta=166.3$, 159.2, 158.5, 138.7, 131.7, 108.1, 107, 106.5, 101.5, 78, 75.5, 69.6, 55.6, 52 ppm; IR (KBr): $\tilde{\nu}=3285$ (m), 2909 (w), 2113 (w), 1713 (m), 1600 (s), 1465 (m), 1437 (s), 1386 (m), 1330 (s), 1268 (m), 1243 (m), 1185 (s), 1160 (m), 1060 (m), 1050 (m), 1013 (m), 830 (m), 763 (m), 678 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 564.2 (8) $[M]^+$, 365.2 (15.51), 199 (100), 128 (64.4); elemental analysis (%) calcd for $C_{34}H_{28}O_8$: C 72.33, H 5.00; found: C 72.21, H 4.89.

Methyl 3,5-bis[(3,5-bis{[3,5-bis(2-propynyloxy)benzyl]oxy}benzyl)oxy]benzoate (Acet$_8$-G3-COOCH$_3$) (12): A solution of methyl 3,5-dihidroxybenzoate (**1**; 0.025 g, 0.15 mmol), 1,3-bis{[3,5-bis(2-propynyloxy)benzyl]oxy}-5-(bromoethyl)benzene (**8**; 0.184 g, 0.3 mmol), K_2CO_3 (0.165 g, 1.2 mmol), and [18]crown-6 (10 mg) in acetone (8 mL) was heated to reflux under nitrogen for 48 h. The reaction mixture was then evaporated to dryness and partitioned between water and dichloromethane. The organic layer was dried over Na_2SO_4, evaporated, and the solid crystallized in methanol to give the product as white crystals (0.165 g, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=7.27$ (s, 2H), 6.76 (t, J(H,H) = 2.4 Hz, 1H), 6.67 (d, J(H,H) = 2.4 Hz, 8H), 6.65 (d, J(H,H) = 2.4 Hz, 4H), 6.56 (t, J(H,H) = 2.4 Hz, 4H), 6.53 (t, J(H,H) = 2.4 Hz, 2H), 4.99 (s, 12H), 4.66 (d, J(H,H) = 2.4 Hz, 16H), 3.91 (s, 3H), 2.51 ppm (t, J(H,H) = 2.4 Hz, 8H); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 20 °C, TMS) $\delta=159.8$, 158.9, 139.6, 139.3, 116.5, 107.1, 101.6, 79.6, 79.1, 79, 78.3, 77.8, 69.6, 56, 49, 48.6, 48.2, 47.7, 47.3 ppm; IR (KBr): $\tilde{\nu}=3287$ (m), 2905 (w), 2115 (w), 1709 (m), 1601 (s), 1465 (m), 1427 (s), 1383 (m), 1310 (s), 1265 (m), 1231 (m), 1187 (s), 1161 (m), 1056 (m), 1014 (m), 818 (m), 762 cm^{-1} (m); MS (ESI): m/z (%): 1222 (100), 1204.9 (6) $[M]^+$; elemental analysis (%) calcd for $C_{74}H_{60}O_{16}$: C 73.74, H 5.02; found: C 73.62, 5.01.

General procedure (A): **copper(I)-catalyzed Huisgen reaction (azyde–alkyne cycloaddition; CuAAC)**: The corresponding acetylenic core (50, 25, and 12.5 mol % for the first-, second-, and third-generation compounds, respectively), $CuSO_4{\cdot}5H_2O$ (5 mol %), and sodium ascorbate (10 mol %) were added to a solution of the azide (100 mol %) in the minimum amount of THF/H_2O (1:1). The reaction mixture was stirred for 3 h, the THF was evaporated under vacuum, and the residue was partitioned between water and $CHCl_3$. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The crude products (usually brown oils) were washed with methanol under reflux, cooled to room temperature to form brown waxy solids, filtered, and washed again with methanol. The products appeared to be pure as shown by NMR spectroscopic measurements and TLC ($CHCl_3$/methanol, 20:1)

Pyr$_2$-G1-COOCH$_3$ (5): The product was synthesized according to general procedure A from azide **4** (0.34 g, 1.13 mmol) and acetylenic core **3** (0.138 g, 0.57 mmol) and obtained as a brown waxy solid (0.45 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=8.21$–8.12 (m, 6H), 8.08 (d, J(H,H) = 8 Hz, 4H), 8.02–7.94 (m, 6H), 7.79 (d, J(H,H) = 7.8 Hz, 2H), 7.43 (s, 2H), 7.25 (d, J(H,H) = 2.2 Hz, 2H), 6.76 (s, 1H), 5.11 (s, 4H), 4.34 (t, J(H,H) = 8 Hz, 4H), 3.88 (s, 3H), 3.35 (t, J(H,H) = 8 Hz, 4H), 2.09–1.99 (m, 4H), 1.93–1.82 ppm (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta=166.3$, 165.6, 135.4, 132.1, 131.3, 130.7, 129.9, 128.4, 127.4, 127.1, 126.7, 125.8, 124.9, 124.7, 123.0, 122.6, 62.2, 52.4, 50.3, 32.8, 30.1, 28.4 ppm; IR (KBr): $\tilde{\nu}=3036$ (w), 2937 (w), 2861 (w), 1728 (m), 1594 (m), 1457 (m), 1436 (m) 1316 (d), 1234 (m), 1170 (s), 1041 (s), 840 (s), 768 cm^{-1} (m); MS (ESI): m/z (%): 881.27 (41) $[M+K]^+$, 865.36 (100) $[M+Na^+]$, 842.36 (13) $[M]^+$; elemental analysis (%) calcd for $C_{54}H_{46}N_6O_4$: C 76.94, H 5.50, N 9.97; found: C 77.17, H 5.52, N 10.

Pyr$_4$-G2-COOCH$_3$ (9): The product was synthesized according to general procedure A from azide **4** (0.2 g, 0.67 mmol) and acetylenic core **8** (0.095 g, 0.17 mmol) and obtained as a brown waxy solid (0.27 g, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=8.15$–8.09 (m, 16H), 8.06–8.00 (m 8H), 7.98–7.89 (m, 8H), 7.73 (d, J(H,H) = 7.8 Hz, 4H), 7.36 (s, 4H), 7.22 (d, J(H,H) = 2.3 Hz, 2H), 6.72–6.79 (m, 1H), 6.60 (d, J(H,H) = 2 Hz, 4H), 6.54–6.49 (m, 2H), 5.04 (s, 8H), 4.92 (s, 4H), 4.24 (t, J(H,H) = 8 Hz, 8H), 3.85 (s, 3H), 3.26 (t, J(H,H) = 8 Hz, 8H), 2.02–1.88 (m, 8H), 1.86–1.72 ppm (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta=166.6$, 159.4, 143.5, 139, 135.5, 131.9, 131.2, 130.7, 129.8, 128.4, 127.4, 127.3, 127, 126.6, 125.8, 124.9, 124.8, 122.9, 122.8, 108.4, 107, 106.5, 101.4, 76.6, 69.9, 61.9, 52.4, 50.6, 50.2, 32.7, 30, 28.3 ppm; IR (KBr): $\tilde{\nu}=3036$ (w), 2935 (w), 1717 (m), 1594 (s), 1436 (m), 1299 (m), 1231 (m), 1157 (s), 1043 (s), 844 (s), 768 (m), 708 (m), 679 (m), 587 cm^{-1} (m); MS (ESI): m/z (%): 1800.6 (10 %) $[M+K]^+$, 1784.7 (27) $[M+Na]^+$, 1762.6 (10), 1447.5 (37), 1003.4 (39), 987.4 (100), 855.4 (40), 685.6 (64), 569.5 (46); elemental analysis (%) calcd for $C_{114}H_{96}N_{12}O_8$: C 77.71, H 5.49, N 9.54; found: C 77.32, H 5.45, N 9.46.

Pyr8-G3-COOCH$_3$ (13): The product was synthesized according to general procedure A from azide **4** (0.1 g, 0.33 mmol) and acetylenic core **12** (0.050 g, 0.04 mmol) and was obtained as a brown waxy solid (0.130 g, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=8.1$–8.03 (m, 24H), 8.0–7.97 (m, 16H), 7.93–7.86 (m, 24H), 7.67 (d, J(H,H) = 8 Hz, 8H), 7.27 (s, 8H), 7.20 (d, J(H,H) = 2 Hz, 2H), 6.67 (s, 1H), 6.56–6.55 (m, 12), 6.47 (s, 6H), 4.98 (s, 16H), 4.88 (s, 4H), 4.85 (s, 8H), 4.15 (t, J(H,H) = 8 Hz, 16H), 3.79 (s, 3H), 3.20 (t, J(H,H) = 8 Hz, 16H), 1.91–1.84 (m, 16H), 1.76–1.68 ppm (m, 16H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): $\delta=159.5$, 159.1, 143.3, 139, 138.6, 135.2, 130.9, 130.4, 129.5, 128.1, 127.1, 126.8, 126.3, 125.5, 124.6, 124.4, 122.7, 122.4, 106, 101, 69.4, 61.6, 50.6, 49.8, 32.3, 29.6, 29.5, 27.9 ppm; IR (KBr): $\tilde{\nu}=3025$ (w), 2920 (w), 2868 (w), 2366 (w), 1720 (w), 1593 (s), 1452 (m), 1369 (w), 1296 (w), 1155 (s), 1040 (m), 837 (m), 764 (w), 706 (w), 675 cm^{-1} (w); MS (ESI): m/z (%): 3664.6 (10), 2464 (20), 1935.7 (26), 1863.5 (100), 1843.5 (17), 1823.1 (13); elemental analysis (%) calcd for $C_{234}H_{196}N_{24}O_{16}$: C 78.06, H 5.49, N 9.34; found: C 77.82, H 5.47, N 9.29.

Pyr$_2$-G1-COOCH$_3$ (18): The product was synthesized according to general procedure A from azide **4** (0.25 g, 0.84 mmol) and acetylenic core **7** (0.37 g, 0.42 mmol) and obtained as a brown waxy solid (0.58 g, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): $\delta=8.22$–8.06 (m, 10H), 8.03–7.91 (m, 6H), 7.80 (d, J(H,H) = 7.8 Hz, 2H), 7.46 (s, 2H), 6.59 (s, 2H), 6.53 (s, 1H), 5.09 (s, 4H), 4.46 (s, 2H), 4.35 (t, J(H,H) = 6.2 Hz, 4H), 3.35 (t, $J=7.5$ Hz, 4H), 2.1–2.0 (m, 4H), 1.90–1.82 ppm (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$, 20 °C, TMS): $\delta=159.1$, 139.5, 139.3, 135.2, 131, 130.4, 129.6, 129.5, 129.3, 128.1, 127, 126.4, 125.6, 124.6, 124.5, 122.3, 122.7, 107.6, 101.5, 61.7, 49.8, 45.9, 32.3, 29.7, 28 ppm; IR (KBr): $\tilde{\nu}=3045$ (m), 2954 (s), 1600 (s), 1461 (s), 1166 (s), 1050 cm^{-1} (m); MS (ESI): m/z (%): 899.4 (90) $[M+Na]^+$, 876.5 (22) $[M]^+$, 855.45 (100), 833.45 (26), 797.5(96); elemental analysis (%) calcd for $C_{53}H_{45}N_6O_2Br$: C 72.51, H 5.17, N 9.57; found: C 72.51, H 5.07, N 9.33.

Pyr$_2$-G1-(styrylpyrydinium) bromide (20): A solution of **19** (0.083 g, 0.33 mmol) and **18** (0.29 g, 0.33 mmol) in $CHCl_3$ (20 mL) was heated to reflux for 24 h. The solvent was evaporated to dryness and the crude product purified by column chromatography on silica gel with dichloromethane/methanol of increasing polarity (20:1, 10:1, 5:1) as the eluent (0.25 g, 67 %). $R_f=0.22$ (dichloromethane/methanol, 20:1, final product is the red spot); ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.78$ (d, *J*(H,H) = 4 Hz, 2 H), 8.09–7.85 (m, 16 H), 7.67 (d, *J*(H,H) = 7.8 Hz, 2 H), 7.36–7.20 (m, 6 H) , 6.84 (s, 2 H), 6.57–6.38 (m, 5 H), 5.64–5.58 (m, 2 H), 5.08 (s, 4 H), 4.27 (t, *J* = 4 Hz, 4 H), 3.30 (q, *J*(H,H) = 4 Hz, 4 H), 3.19 (t, 8 Hz, 4 H), 2.0–1.90 (m, 4 H), 1.78–1.66 (m, 4 H), 1.17–1.08 ppm (m, 6 H); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta=159.6$, 153.6, 149.8, 142.7, 135.7, 131.2, 130.8, 130.6, 129.6, 128.3, 127.4, 127.2, 127, 126.5, 125.8, 124.7, 123.1, 121.9, 121.5, 115.4, 111.3, 108.2, 61.8, 50.5, 50.1, 44.6, 32.6, 30.2, 28.4, 12.8 ppm; IR (KBr): $\tilde{\nu}=3031$ (w), 2929 (w), 2852 (w), 1634 (m), 1571 (s), 1518 (m), 1449 (m), 1401 (w), 1346 (m), 1321 (m), 1267 (m), 1149 (s), 1043 (m), 842 cm^{-1} (s); MS (ESI): *m*/*z* (%): 1049.5 (100) $[M]^+$, 876.3 (8), 751.4 (38), 750.4 (67), 712.4 (12), 534.3 (55); elemental analysis (%) calcd for $C_{70}H_{65}BrN_8O_2$: C 74.39, H 5.80, N 9.91; found: C 73.97, H 5.73, N 9.87.

Pyr$_2$-G1-*N*-propylamine (18 a): Compound **18** (0.09 g, 0.1 mmol), was dissolved in propylamine (2 mL) and CHCl$_3$ (2 mL) and stirred for 4 h at room temperature. The reaction mixture was evaporated to dryness and the residue was dissolved in CHCl$_3$ (30 mL) and washed with NaHCO$_3$ (sat. solution, 4 × 100 mL). The organic layer was dried over Na$_2$SO$_4$ and evaporated. The product was used for the next step without further purification. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.29$–7.89 (m, 16 H), 7.74 (d, *J*(H,H) = 7.8 Hz, 2 H), 7.40 (s, 2 H), 6.56 (s, 2 H), 6.49 (s, 1 H), 5.09 (s, 4 H), 4.25 (t, *J*(H,H) = 8 Hz, 4 H), 3.67 (s, 2 H), 3.27 (t, *J*(H,H) = 8 Hz, 4 H), 2.52 (t, *J*(H,H) = 6 Hz, 2 H), 2.06–1.85 (m, 4 H), 1.86–165 (m, 4 H), 1.56–1.40 (m, 2 H), 0.89 ppm (t, *J*(H,H) = 6 Hz, 3 H).

Pyr$_2$-G1-*N*-propylamine-*N*-nitrobenzofurazan (20): Compound **18 a** (0.083 g, 0.097 mmol) and 4-chloro-7-nitrobenzofurazan (**17**; 0.039 g, 0.194 mmol) were dissolved in CHCl$_3$ and stirred overnight at room temperature. DIPEA (2 drops) was added to the solution, and the reaction mixture was stirred for 1 h. The reaction mixture was washed with NaHCO$_3$ and brine. The organic layer was dried over Na$_2$SO$_4$ and evaporated under vacuum. The crude product was purified by column chromatography on neutral aluminum oxide eluting with CHCl$_3$ to yield a dark orange gum (0.092 g, 92 %). ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.09$–7.84 (m, 17 H), 7.70 (d, *J*(H,H) = 7.8 Hz, 2 H), 7.45 (s, 2 H), 7.21 (d, *J*(H,H) = 7.8 Hz, 1 H), 6.49 (s, 1 H), 6.31 (s, 2 H), 5.02 (s, 4 H), 4.30 (t, *J*(H,H) = 7.1 Hz, 4 H), 3.74–3.67 (m, 2 H), 3.25 (t, *J*(H,H) = 7.6, 4 H), 2.04–1.93 (m, 4 H), 1.85–1.71 (m, 4 H), 1.69–1.60 (m, 2 H), 1.30–1.18 (m, 2 H), 0.92 ppm (t, *J*(H,H) = 7.4 Hz, 3 H); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta=159.8$, 144.7, 143.3, 142.3, 137.2, 135.5, 135, 131.9, 131.1, 130.6, 130, 129.6, 128.3, 128.1, 127.3, 127.2, 127.1, 126.6, 125.9, 124.9, 124.7, 122.9, 122.7, 122.3, 105.6, 101.8, 100.9, 62, 56.5, 56.1, 50.3, 32.7, 30.1, 29.9, 28.4, 11.2 ppm; IR (KBr): $\tilde{\nu}=3030$ (w), 2925 (w), 2852 (w), 1636 (m), 1570 (s), 1518 (m), 1446 (m), 1401 (w), 1380 (m) 1345 (m), 1328 (m), 1267 (m), 1149 (s), 1043 (m), 842 (s), 636 (m), 530 cm^{-1} (m); MS (ESI): *m*/*z* (%): 1041.5 (15) $[M-\mathrm{Na}^+]$, 1018.4 (100) $[M]^+$, 976.3 (34), 714.4 (70), 614.7 (37), 302.8 (60); elemental analysis (%) calcd for $C_{62}H_{54}N_{10}O_5$: C 73.07, H 5.34, N 13.74; found: C 72.87, H 5.29, N 13.69.

Pyr$_4$-G2-Br (11 a): The product was synthesized according to general procedure A from azide **4** (0.29 g, 0.97 mmol) and acetylenic core **11** (0.148 g, 0.24 mmol) and obtained as a brown waxy solid (0.416 g, 95 %). ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.13$–7.80 (m, 32 H), 7.70 (d, *J*(H,H) = 7.8 Hz, 4 H), 7.32 (s, 4 H), 6.67–6.36 (m, 9 H), 5.03 (s, 8 H), 4.87 (m, 4 H), 4.34 (s, 2 H), 4.19 (t, *J*(H,H) = 7.0 Hz, 8 H), 3.22 (t, *J*(H,H) = 7.45 Hz, 8 H), 1.97–1.85 (m, 8 H), 1.81–1.69 ppm (m, 8 H); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta=159.4$, 159.2, 143.2, 138.9, 135.2, 131, 130.4, 129.5, 128.1, 127.1, 126.8, 126.4, 125.5, 124.6, 124.4, 122.7, 122.4, 106.1, 101, 69.4, 67.7, 61.6, 49.7, 32.2, 30.1, 29.6, 27.9, 25.4 ppm; IR (KBr): $\tilde{\nu}=3043$ (m), 2960 (s), 1605 (s), 1461 (s), 1162 (s), 1049 cm^{-1} (m); MS (ESI): *m*/*z* (%): 1716.6 (8), 1567.2 (24), 1417.6 (47), 1267.5 (39), 1118 (20), 685.6 (28), 569.5 (20), 554.45 (74), 552.4 (100); elemental analysis (%) calcd for $C_{113}H_{95}BrN_{12}O_6$: C 75.53, H 5.33, N, 9.35; found C 75.42, H 5.30, N 9.28.

Pyr$_4$-G2-(styrylpyridinium) bromide (21): Compound **11 a** (0.44 g, 0,24 mmol) and **19** (0.061 g, 0.24 mmol) were dissolved in CHCl$_3$ (10 mL) and heated to reflux for 24 h. The solvent was evaporated, and the crude product was purified by column chromatography on neutral aluminum oxide, starting the elution with CHCl$_3$ then increasing the polarity (CHCl$_3$/methanol 30:1, 20:1, 10:1) to yield a red solid (0.38 g, 76 %). $R_f=0.34$ (CHCl$_3$/MeOH, 20:1, red spot on an aluminum oxide TLC plate); ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.72$–8.66 (bs, 2 H), 8.12–7.83 (m, 32 H), 7.67 (d, *J*(H,H) = 7.8, 4 H), 7.47 (s, 4 H), 7.30–7.21 (m, 5 H), 6.78–6.36 (m, 10 H), 5.57–5.46 (m, 2 H), 4.99 (s, 8 H), 4.93 (m, 4 H), 4.19 (t, *J*(H,H) = 8 Hz, 8 H), 3.33–3.24 (m, 4), 3.18 (t, *J*(H,H) = 8 Hz, 8 H), 1.95–1.83 (m, 8 H), 1.78–1.66 (m, 8 H), 1.09 ppm (t, *J*(H,H) = 7 Hz, 6 H); ^{13}C NMR (50 MHz, [D$_6$]DMSO, 20 °C, TMS): $\delta=160.2$, 159.6, 143.6, 142.8, 139.5, 136.7, 131.2, 130.7, 129.6, 128.9, 128.4, 127.8, 127.6, 126.9, 126.5, 125.3, 124.5, 123.8, 111.8, 107.1, 79.7, 69.8, 61.81, 49.8, 44.3, 32.4, 30.3, 28.8, 13.1 ppm; IR (KBr): $\tilde{\nu}=3036$ (w), 2929 (w), 2853 (w), 1639 (m), 1568 s), 1520 m), 1446 (m), 1407w), 1342(m), 1321(m), 1268(m), 1149 (s), 1041(m), 835 cm^{-1}(s); MS (ESI): *m*/*z* (%): 1967.9 (90), 1967.91 (63) $[M^+]$, 1669.8 (100), 1370.6 (62), 1070.6 (26), 1049.6 (19), 996.1 (25); elemental analysis (%) calcd for $C_{130}H_{115}BrN_{14}O_6$: C 76.19, H 9.57, N 9.57; found: C 75.96, H 9.46, N 9.61.

Acet8-G3-(styrylpyridinium) bromide (22 b): Compound **22 a** (0.15 g. 0.118 mmol) and **19** (0.03 g, 0.118 mmol) were dissolved in toluene (10 mL) and heated at 80 °C overnight. The toluene was evaporated and the residue was purified by column chromatography on neutral aluminum oxide, starting the elution with CHCl$_3$ increasing the polarity (CHCl$_3$/methanol 20:1) to yield a red waxy solid (0.15 g, 83 %). $R_f=0.1$ (CHCl$_3$/MeOH, 20:1, red spot on an aluminum oxide TLC plate); ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=9.0$ (d, *J*(H,H) = 6.4 Hz, 2 H), 7.52 (d, *J*(H,H) = 6.4 Hz, 2 H), 7.41–7.36 (m, 3 H), 6.83 (d, *J*(H,H) = 1.6 Hz, 2 H), 6.64–6.55 (m, 15 H), 6.5–6.42 (m, 7 H), 5.77 (s, 2 H), 4.93 (s, 4 H), 4.91 (s, 8 H), 4.60 (d, *J*(H,H) = 2.8 Hz, 16 H), 3.37 (q, *J*(H,H) = 6.8 Hz, 4 H), 2.51 (t, *J*(H,H) = 2.4 Hz, 8 H), 1.16 ppm (t, *J*(H,H) = 2.4 Hz, 6 H); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta=160$, 159.6, 158.6, 149.9, 143.3, 139.4, 139.1, 136, 130.9, 122.2, 121.6, 115.8, 111.4, 108.1, 106.8, 101.7, 78.4, 77.8, 77.2, 76.6, 76, 69.7, 56, 44.7, 12.8 ppm; IR (KBr): $\tilde{\nu}=3277$ (s), 2963 (w), 2919 (w), 2863 (w), 2112 (w), 1591 (s), 1518 (m), 1451 (m), 1323 (w), 1150 (s), 1043 (m), 953 (w), 831 (w), 752 (w), 674 (w), 640 cm^{-1} (w); MS (ESI): *m*/*z* (%): 1610.3 (5), 1450.36 (4), 1412.4 (100) $[M]^+$, 1321.8 (5); elemental analysis (%) calcd for $C_{90}H_{79}BrN_2O_{14}$: C 72.43, H 5.34, N 1.88; found : C 72.14, H 5.32, N 1.91.

Pyr$_8$-G3-(styrylpyridinium) bromide (23): The product was synthesized according to general procedure A from azide **4** (0.079 g, 0.026 mmol) and acetylenic core **22 b** (0.05 g, 0.033 mmol). The crude product was purified by column chromatography on neutral aluminum oxide, eluting with CHCl$_3$/methanol (20:1) to yield a red waxy solid (0.112 g, 87 %). $R_f=0.32$ (CHCl$_3$/MeOH, 20:1, red spot on an aluminum oxide TLC plate); ^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): $\delta=8.51$ (d, *J*(H,H) = 6 Hz, 2 H), 8.0–7.92 (m, 24 H), 7.90–7.88 (m, 16 H), 7.87–7.81 (m, 24 H), 7.56 (d, *J*(H,H) = 8 Hz, 8 H), 7.3–7.23 (m, 10 H), 7.91 (d, *J*(H,H) = 8.4 Hz, 2 H), 7.0–6.96 (m, 3 H), 6.63 (s, 1 H), 6.55 (d, *J*(H,H) = 10.4 Hz, 12 H), 4.43 (d, *J*(H,H) = 6.4 Hz, 6 H), 6.37 (d, *J*(H,H) = 12.8 Hz, 2 H), 6.15 (d, *J*(H,H) = 15.6 Hz, 1 H), 5.40 (bs, 2 H), 4.90–4.80 (m, 28 H), 4.04 (t, *J*(H,H) = 6.8 Hz, 16 H), 3.20–3.13 (m, 4 H), 3.05 (t, *J*(H,H) = 6.8 Hz, 16 H), 1.79–1.71 (m, 16 H), 1.63–1.56 (m, 16 H), 0.99 ppm (t, *J*(H,H) = 7.2 Hz, 6 H); ^{13}C NMR (50 MHz, CDCl$_3$, 20 °C, TMS): $\delta=159.7$, 159.4, 143.3, 139.4, 135.6, 131.2, 130.6, 129.6, 128.3, 127.3, 127, 126.5, 125.8, 124.7, 123, 106.4, 101.2, 61.8, 50, 32.6, 30, 28.3 ppm; IR (KBr): $\tilde{\nu}=3020$ (w), 2919 (w), 2851 (w), 1597, (m), 1451 (m), 1323 (w), 1149 (s), 1037 (m), 841 (m), 746 cm^{-1} (w); MS (ESI): *m*/*z* (%): 1903.4 (6) $[M^{2+}]$, 1734.8 (5), 1610.2 (6), 1505.3 (5), 1444.3 (16), 1411.2 (100), 1269.6 (5) $[M^{3+}]$, 1221.8 (21), 1045.8 (14); elemental analysis (%) calcd for $C_{250}H_{215}N_{26}O_{14}Br$: C 77.24, H 5.57, N 9.37; found C 76.99, H 5.49, N 9.41.

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[26] The UV and fluorescence spectra of **5**, **14**, and **15** in solution, UV and fluorescence spectra of **15** (cast-film), the derivation of Equation (3), and general remarks on the experimental details, synthesis, and characterization of **4**, **14**, **15**, and **19** are given in the Supporting Information.

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