

Photoluminescent Energy Transfer from Poly(phenyleneethynylene)s to Near-Infrared Emitting Fluorophores

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ABSTRACT: Photoluminescent energy transfer was investigated in conjugated polymer-fluorophore blended thin films. A pentyene-containing poly(phenyleneethynylene) was used as the energy donor, and 13 fluorophores were used as energy acceptors. The efficiency of energy transfer was measured by monitoring both the quenching of the polymer emission and the enhancement of the fluorophore emission. Near-infrared emitting squaraines and terylenes were identified as excellent

energy acceptors. These results, where a new fluorescent signal occurs in the near-infrared region on a completely dark background, offer substantial possibilities for designing highly sensitive turn-on sensors. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 3382–3391, 2010

KEYWORDS: conjugated polymers; fluorescence; sensors; thin films

INTRODUCTION The highly efficient energy transfer¹ and exciton migration processes² in conjugated polymers can be exploited in various electronic applications^{3–11} and in amplifying sensor responses.^{12–19} Highly sensitive, amplified quenching of polymer emission has been accomplished with various quenchers in solution as well as in the solid state.^{20–25} Applications of this amplified quenching include the detection of chemical and biological analytes,^{26–38} and explosives.³⁹

In contrast to turn-off sensors based on amplified polymer quenching, turn-on sensors have the advantage of potentially being even more sensitive and selective,^{40,41} especially if the new signal can be generated on a completely dark background. Some examples of turn-on sensors have been developed previously.^{42–45} In many of these sensors, the emission spectrum of the donor overlaps with the emission spectrum of the acceptor. This overlap leads to decreased sensitivity in turn-on sensory applications, as even in the absence of the acceptor there is background donor emission in the same spectral region, and hence not the desired completely dark background.

Recent results from our group have demonstrated superior energy transfer with reduced spectral overlap between the absorption spectra of the streptavidin-functionalized fluorophore acceptors and the emission spectrum of the biotin-functionalized poly(phenyleneethynylene) (PPE) donor.⁴⁶ Sensors with completely separated donor and acceptor emissions, which rely on electronic exchange mechanisms, have the potential to exhibit significantly enhanced sensitivity, as

the emission of the acceptor occurs on a dark background, without interfering donor emission.

Additionally, turn-on sensors that display a new fluorescence emission in the near-infrared (NIR) region (650–900 nm) are highly desirable for biological applications.^{47,48} Biological chromophores exhibit low absorption and auto-fluorescence in this spectral region, which allows photons to penetrate biological tissue.⁴⁹ Some applications of NIR fluorophores in biological imaging have been reported^{50–55}; however, the use of conjugated polymers as energy donors in combination with NIR energy acceptors allows for highly amplified fluorescence emission in a spectral region that is free of interfering signals (neither the polymer donor nor biological analytes fluoresce in this region).

We report herein a thorough investigation of the energy transfer between a conjugated PPE and 13 commercially available and readily-synthesized fluorophores. These compounds have absorption maxima ranging from 537 to 686 nm, with many of the compounds absorbing and fluorescing in the NIR region. We show highly efficient energy transfer from the PPE to the fluorophores, with nearly 100-fold fluorescence amplification in the NIR region from exciting the PPE compared to exciting a squaraine chromophore directly.

EXPERIMENTAL

Spectral grade chloroform and *n*-butanol were obtained from Mallinckrodt Company. Anhydrous toluene, benzene, and

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diisopropylamine were purchased from Aldrich Chemical Company, and were used as received. Ethanol was obtained from Pharmo-Aaper Company. 1,4-diethynylbenzene purchased from Alfa Aesar was purified by chromatography on silica gel before polymerization. Rhodamine 6G (**2a**), 1,1',3,3,3',3'-hexamethylindodicarbocyanine iodide (**3b**), and Nile Red (**4**) were purchased from Aldrich. Sulforhodamine 101 (**2b**) and rhodamine 800 (**2c**) were obtained from Molecular ProbesTM. 1,1'-Diethyl-3,3,3',3'-tetramethylindodicarbocyanine iodide (**3a**) was obtained from Fluka. Oxazine 170 (**5**) was obtained from Acros. 3-Benzyloxyaniline and 1,8-bis(dimethylamino)naphthalene were obtained from Sigma-Aldrich. *tert*-Butyl bromoacetate, cyclohexene, and 3,4-dihydroxycyclobut-3-ene-1,2-dione were obtained from Alfa Aesar. 10% palladium on carbon was obtained from Acros. Trifluoroacetic acid was obtained from Oakwood Products.

Polymer **1** ($M_n = 88,400$, PDI = 2.3)⁵⁶ and polymer **9**⁵⁷ were synthesized according to previously reported procedures.

The synthesis of two squaraine fluorophores, 1,3-bis[4-(dimethylamino)phenyl]-2,4-dihydroxycyclobutenediylum dihydroxide (**6a**) and 1,3-bis[4-[bis(2-methylpropyl) amino]-2,6-dihydroxyphenyl]-2,4-dihydroxy cyclobutenediylum (**6b**) was adapted from literature procedures,⁵⁸ and purified further by column separation after recrystallization. Compound **6c** was synthesized according to literature procedures.^{59,60}

The synthesis of terrylene compounds **7** was accomplished according to literature procedures.⁶¹ Known compounds **7b** and **7c** were synthesized from compound **7a** using procedures that were developed by Müllen and coworkers.⁶²

RESULTS AND DISCUSSION

Materials

The photophysical spectra and properties of polymer **1** are summarized in Figure 1. All of the properties and responses of polymers **1a** and **1b** are identical (absorption and emission spectra, quantum yields, lifetimes) and these polymers are therefore utilized interchangeably. Interestingly, the results described in this article are not dependent upon the minor spatial perturbations that will exist between these polymers.

The molecular structures of the fluorophores used are shown in Chart 1, and their photophysical properties are summarized in Table 1. The wide variety of fluorophores investigated includes near-infrared emitting squaraine compounds **6** and terrylene compounds **7**. Squaraine compounds have characteristic narrow absorption and emission bands with high extinction coefficients.^{63,64} They have been utilized in a variety of applications, including as chemosensors for metal ions^{65–68} and thiols,⁶⁹ as indicators of membrane polarity,⁷⁰ and as guests encapsulated in aromatic macrocycles.^{71–73} Squaraines have also been utilized extensively for biological imaging.^{74,75}

The synthesis of terrylenediimide fluorophores **7** is shown in Scheme 1. Terrylene, which was first crystallized by Clar in 1958,⁷⁶ demonstrates a substantial batho-

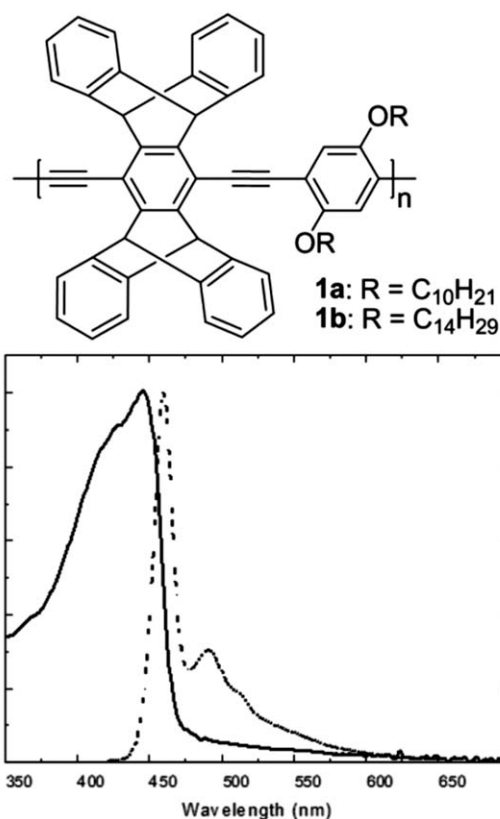


FIGURE 1 The absorption (solid line) and emission (dashed line) spectra of polymer **1a** in spin-cast films (Thin films: $\lambda_{\text{max abs.}} = 446$ nm, $\lambda_{\text{max em.}} = 460$ nm, $\Phi_F = 0.33$, $n(633 \text{ nm}) = 1.66$; chloroform solution: $\lambda_{\text{max abs.}} = 427$ nm, $\lambda_{\text{max em.}} = 453$ nm, $\Phi_F = 0.50$).

chromic shift in its absorption and emission maxima compared to its lower homologues, naphthalene and perylene.⁷⁷ This bathochromic shift has been investigated theoretically.⁷⁸ Terrylene diimides show remarkable photostability,⁷⁹ and have been utilized for a variety of biological applications.^{80–82}

Energy Transfer Studies

Blended thin films of conjugated polymer **1** and the fluorophores were fabricated at a variety of fluorophore concentrations. Efficient energy transfer from the polymer to the fluorophores was observed for NIR-emitting fluorophores, that is, exciting the film at the absorption maximum of the polymer resulted in a new fluorescence emission in the NIR region. The efficiency of the energy transfer from the conjugated polymer to the fluorophores in thin film blends was quantified by two methods. First, the comparison between the fluorophore emission intensity obtained by the excitation of the polymer (I_{AD}) to the emission intensity observed by direct excitation of the fluorophore (I_A) demonstrates photoluminescent energy transfer from the polymer donor to the fluorophore acceptors.

Second, the energy transfer between the conjugated polymer and the fluorophores was quantified by measuring

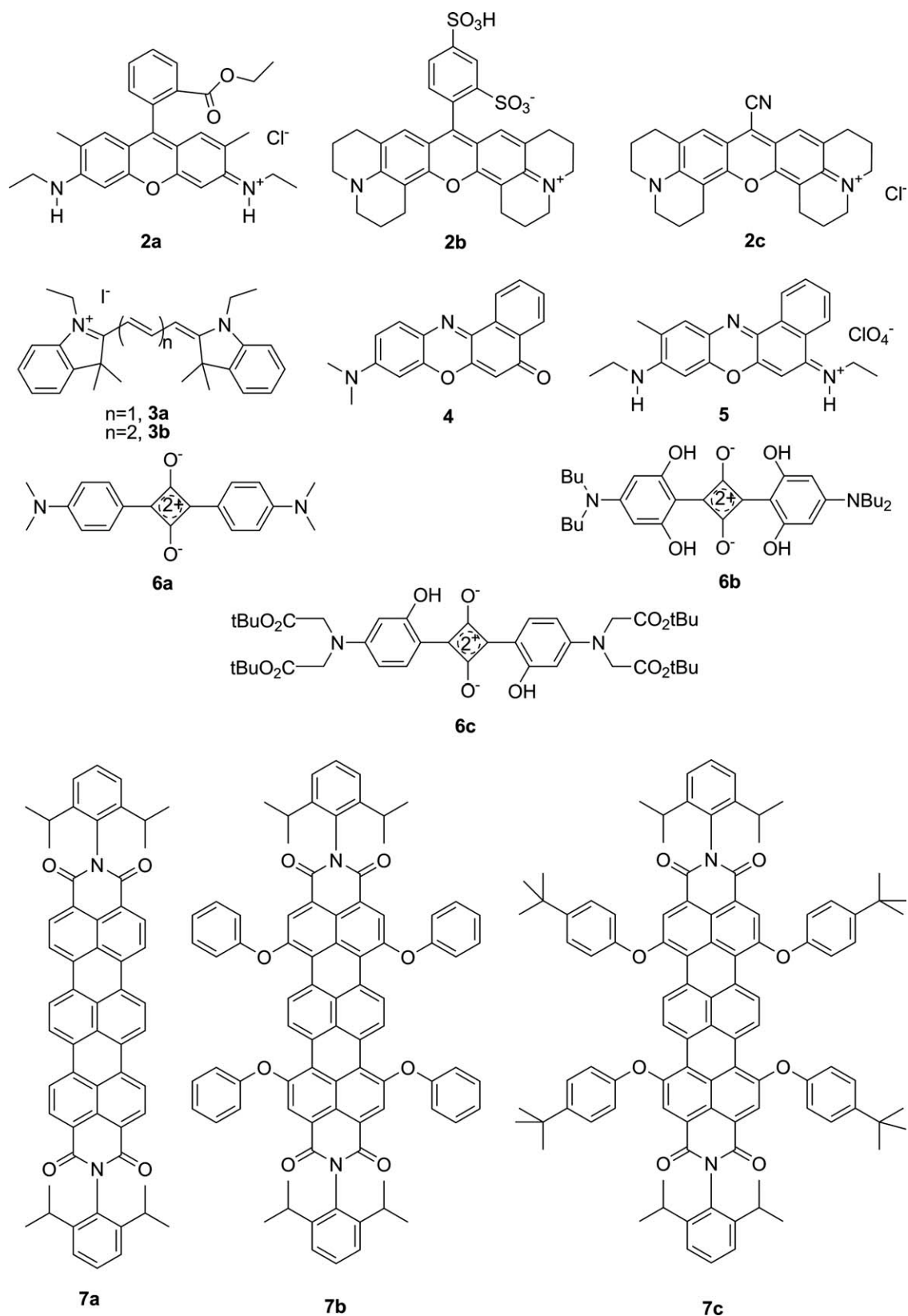


CHART 1 Organic fluorophores used in the energy transfer studies.

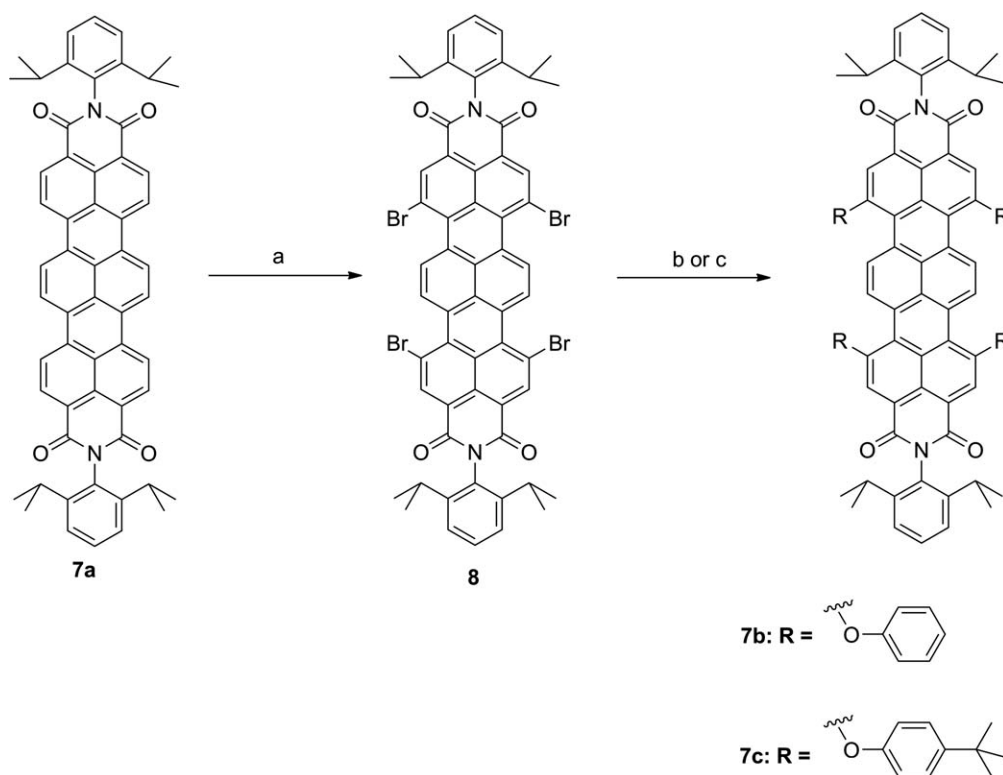
TABLE 1 The Absorption and Fluorescence Maxima of Fluorophores in Spin-Cast PMMA Films and Their Extinction Coefficients^a at Their Absorption Maxima

Fluorophore	λ_{\max} abs. (nm)	λ_{\max} em. (nm)	Extinction Coefficient ϵ (cm ⁻¹ M ⁻¹) $\times 10^4$
2a	552	575	8.75
2b	579	592	6.07
2c	686	707	6.02
3a	556	577	14.00
3b	652	680	20.90
4	537	612	4.76
5	620	638	2.94
6a	635	647	12.30
6b	648	667	27.30
6c	638	645	3.27
7a	671	675	1.22
7b	630, 674	687	0.98
7c	630, 679	760	2.89

^a The extinction coefficients were measured in chloroform.

the fractional quenching of donor emission (E_{exp}) as in Equation 1:

$$E_{\text{exp}} = 1 - F_{\text{DA}}/F_{\text{D}} \quad (1)$$



(a) Br₂, CHCl₃, 100°C, 75% yield; (b) **7b**: phenol, K₂CO₃, N-methyl pyrrolidone (NMP), 80°C, 90% yield; (c) **7c**: *t*-butyl phenol, K₂CO₃, NMP, 80°C, 86% yield

SCHEME 1 Synthesis of terrylene fluorophores **7**.

where F_{DA} and F_{D} are the integrated emission of the donor in the presence and absence of acceptors, respectively. We investigated all of the acceptor fluorophores at 5 and 0.5 wt % (Table 2). For some of the more interesting NIR acceptors, we examined films with extended compositional ranges (Table 3).

The fluorophore emission observed for rhodamine compounds **2** decreases as the absorption maximum of the compounds increases [Fig. 2(A–C)]. Compound **2a**, which has the shortest wavelength absorption maximum, displays the greatest fluorescence enhancement. This result is in accord with Förster energy transfer theory,⁸³ which dictates that the efficiency of energy transfer depends on the spectral overlap between the donor emission and acceptor absorption spectra.

The cyanine compounds **3** show reduced sensitized fluorophore emissions, especially for compound **3b** [Fig. 2(D,E)]. Although thin films with Nile Red **4** show efficient energy transfer [Fig. 2(F)], its cationic analogue oxazine **5** does not function as an efficient energy acceptor [Fig. 2(G)]. The charged nature of compound **5**, as well as its decreased spectral overlap, likely affect the efficiency of energy transfer.

Remarkably, squaraine compounds **6a** and **6b** display a significant amplification of fluorescence from polymer excitation compared to direct fluorophore excitation, with 99-fold and

TABLE 2 Energy Transfer Efficiencies Measured by the Decrease in Polymer Emission (E_{exp}) and the Increase of Fluorophore Emission ($I_{\text{AD}}/I_{\text{A}}$) in Thin Films of Polymer 1 with the Fluorophores at 0.5 and 5 wt % Doping Concentration

Fluorophore	5 wt %		0.5 wt %	
	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$
2a	0.91	76.0	0.99	118.0
2b	0.82	64.2	0.77	84.5
2c	0.97	10.1	0.78	61.7
3a	0.99	6.0	0.89	88.3
3b	0.95	5.4	0.62	66.8
4	0.99	8.4	0.95	64.4
5	0.85	18.7	0.66	^a
6a	0.98	20.5	0.87	98.6
6b	0.99	6.3	0.81	69.5
6c	0.40	53.8	0.09	50.9
7a	0.86	20.6	0.70	41.2
7b	^b	46.6	^b	40.6
7c	0.62	15.0	^b	38.3

^a Fluorophore is not emissive at this concentration.

^b Polymer emission is not quenched at this concentration.

70-fold increases in the fluorophore emission ($I_{\text{AD}}/I_{\text{A}}$) for compounds **6a** and **6b**, respectively, [Fig. 2(H,I)]. This highly efficient energy transfer occurs despite the limited spectral overlap between the polymer emission and the fluorophore absorption spectra. The functionalized squaraine compound **6c** also exhibits substantially enhanced emission from poly-

TABLE 3 Energy Transfer Efficiencies Measured by the Decrease in Polymer Emission (E_{exp}) and the Increase of Fluorophore Emission ($I_{\text{AD}}/I_{\text{A}}$) in Thin Films of Polymer 1 with Fluorophores **6c–7c** at Various Concentrations

Fluorophore	1 wt %		0.1 wt %	
	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$
6c	0.19	46.8	^b	^a
7a	0.79	35.8	0.21	46.3
7b	^b	47.2	^b	26.0
7c	0.16	31.7	^b	33.8

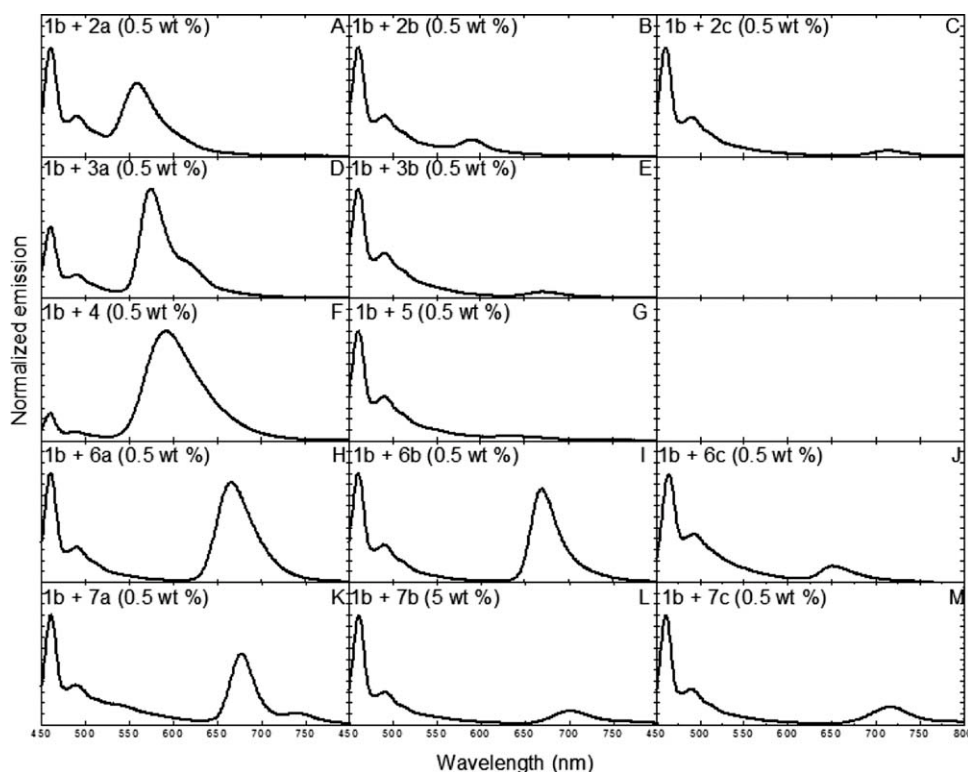
^a Fluorophore is not emissive at this concentration.

^b Polymer emission is not quenched at this concentration.

mer excitation, with up to a 54-fold increase in the fluorophore's emission [Fig. 2(J)]. This NIR-emitting compound is particularly intriguing, as the ester moiety can be readily functionalized^{84,85} and utilized for biological applications such as protein labeling.⁷⁵

Similarly, NIR terrylene fluorophores function as efficient energy acceptors in thin film blends with polymer 1 [Fig. 2(K–M)]. Unsubstituted terrylene diimide **7a** displays a 46-fold amplification of fluorescence from polymer excitation compared to direct fluorophore excitation, which is similar to the amplification observed for the substituted compounds **7b** and **7c**.

The degree of spectral overlap between the polymer's emission spectrum and the fluorophores' absorption spectra is illustrated in Figure 3. This figure illustrates that neither


FIGURE 2 Fluorescence spectra of polymer-fluorophore blends in thin films with polymer excitation at 410 nm. (Y-axis expanded spectra of direct excitation of fluorophores is provided in the Supporting Information).

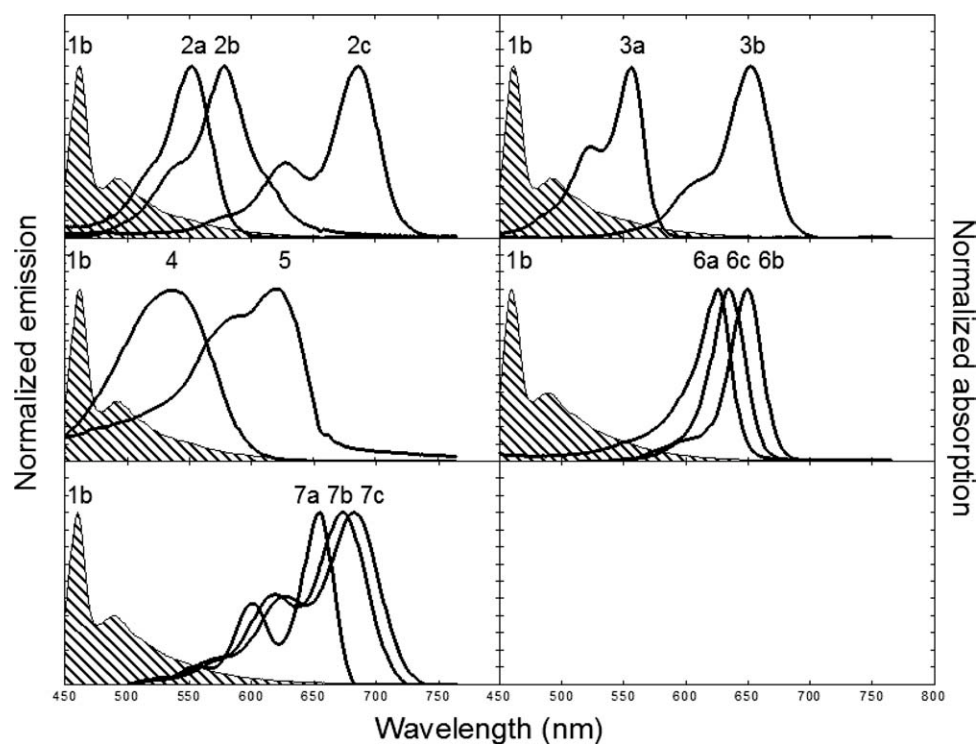


FIGURE 3 Overlaid spectra of the emission of polymer **1** with the absorbance of the fluorophores. The hatched area represents the emission band of the pristine polymer.

the squaraines (compounds **6**) nor the terrylenes (compounds **7**) exhibit appreciable spectral overlap between their absorption spectra and the polymer's emission spectrum, which is in stark contrast to several other fluorophores (compounds **2a**, **2b**, **3a**, **4**, and **5**) which exhibit substantial overlap. Nonetheless, highly efficient energy transfer is observed for all the NIR fluorophores investigated.

These results reveal that both squaraine and terrylene compounds are excellent candidates as energy acceptors with PPE types of donors. The rigidity and compact size of the squaraines allow them to interact well with the planar polymer backbones. The fluorophores can stack close to the polymers, causing more efficient energy transfer through orbital overlap. Moreover, the internal free volumes associated with the pentiptycene in polymer **1** may work as a guiding frame to locate fluorophores close to the polymer backbone. Squaraines have already been shown to interact efficiently with π systems, as well as with iptycene-containing frameworks.⁸⁶ The ability of terrylene fluorophores to function as excellent energy acceptors is likely a result of their ability to π -stack efficiently with the conjugated polymer backbone.⁸¹ The fact that both squaraines and terrylenes display highly amplified NIR emission opens the possibility of using these systems for turn-on biological sensors.

Comparison to a Simple PPE

The performance of pentiptycene-containing polymer **1** was compared to that of a simple PPE, compound **9**.⁵⁷ The photophysical spectra and properties of polymer **9** are summarized in Figure 4. The broad excimer emission (510 nm) in the fluorescence spectrum of polymer **9** in thin films

indicates that aggregation has occurred (this band is absent in the emission spectra of the polymer in chloroform solution).

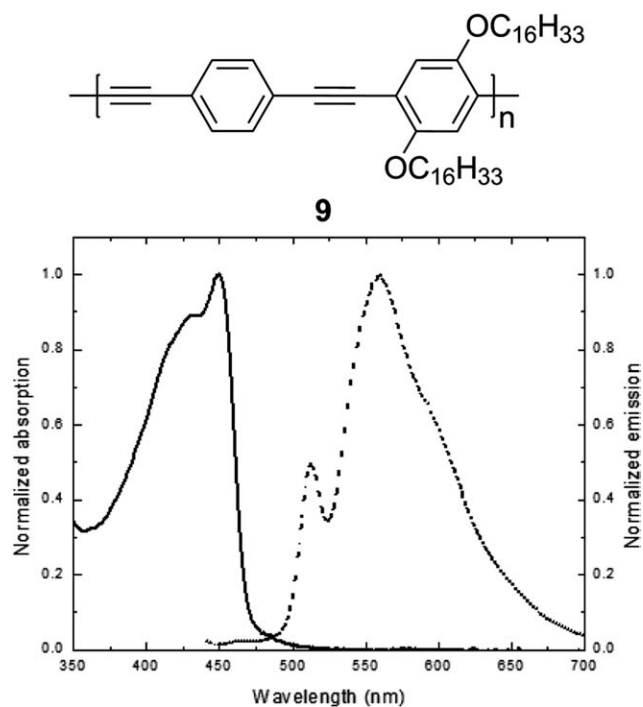


FIGURE 4 The absorption (solid line) and emission (dashed line) spectra of polymer **9** in spin-cast films (Thin films: λ_{\max} abs. = 449 nm, λ_{\max} em. = 463 nm, 511 nm, $\Phi_F = 0.04$, $n(633 \text{ nm}) = 1.57$; chloroform solution: λ_{\max} abs. = 413 nm, λ_{\max} em. = 447 nm, $\Phi_F = 0.41$).

TABLE 4 Energy Transfer Efficiencies Between Polymer **9** and Fluorophores **2-6b** Measured by the Decrease in Polymer Emission (E_{exp}) and the Increase in Fluorophore Emission ($I_{\text{AD}}/I_{\text{A}}$)

	5 wt %		0.5 wt %	
	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$	E_{exp}	$I_{\text{AD}}/I_{\text{A}}$
2a	0.73	14.7	0.52	42.2
2b	0.79	13.5	0.14	47.3
2c	0.37	21.9	b	a
3a	0.84	9.0	0.54	43.0
3b	b	36.9	b	a
4	0.93	16.0	0.53	86.8
5	0.22	56.6	b	a
6a	0.10	a	b	a
6b	0.64	48.1	0.22	91.9

^a Fluorophores were not emissive at this concentration.

^b The polymer emission was not quenched at this concentration.

When compared to polymer **1**, polymer **9** shows less efficient energy transfer in terms of both donor quenching and amplified acceptor emission (Table 4, Fig. 5). The only exceptions are compounds **4** and **6b**, which accomplish comparable energy transfer in blends with both **1** and **9**. The quenching of the emission of polymer **9** with added fluorophore is substantially less than the quenching observed with polymer **1**. One possible reason for the limited quenching in blends of **9** is that phase separation occurs between the polymer and the fluorophores in spin-cast films. The dense packing of the

polymer chains in **9** likely makes it hard to incorporate fluorophores into the polymer matrix. Hence, the fluorophores tend to self-aggregate, and the incorporated fluorophore content decreases. On the other hand, polymer **1**, with the porous internal structure derived from the pentiptycene moieties, prevents phase separation during the spin-casting process and facilitates the entrapment of the fluorophores in close proximity to the polymer backbone.

Electrochemistry

Recent studies have emphasized that photoinduced electron transfer (PET) can compete with energy transfer, and that the relative position of the donor and acceptor frontier orbitals is critical in favoring energy transfer over PET.⁸⁷⁻⁸⁹ When both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of an acceptor are located within the energy range defined by the donor's HOMO-LUMO gap, energy transfer dominates. Alternatively, if the HOMO or the LUMO of the acceptor is outside the donor's HOMO-LUMO gap, photoinduced electron transfer between the donor and the acceptor can occur followed by nonradiative relaxation.⁹⁰⁻⁹² Therefore, the HOMO-LUMO energy levels of the donor should bracket those of the acceptor to minimize the nonradiative loss of excited donor energy.

To estimate HOMO and LUMO levels, the oxidation and reduction potential of fluorophores were obtained by cyclic voltammetry, and the energy levels obtained from the potential differences^{93,94} (electrochemical band gap) were compared to the onset wavelengths of the absorption spectra (optical band gap) (Table 5). The HOMO and LUMO energies

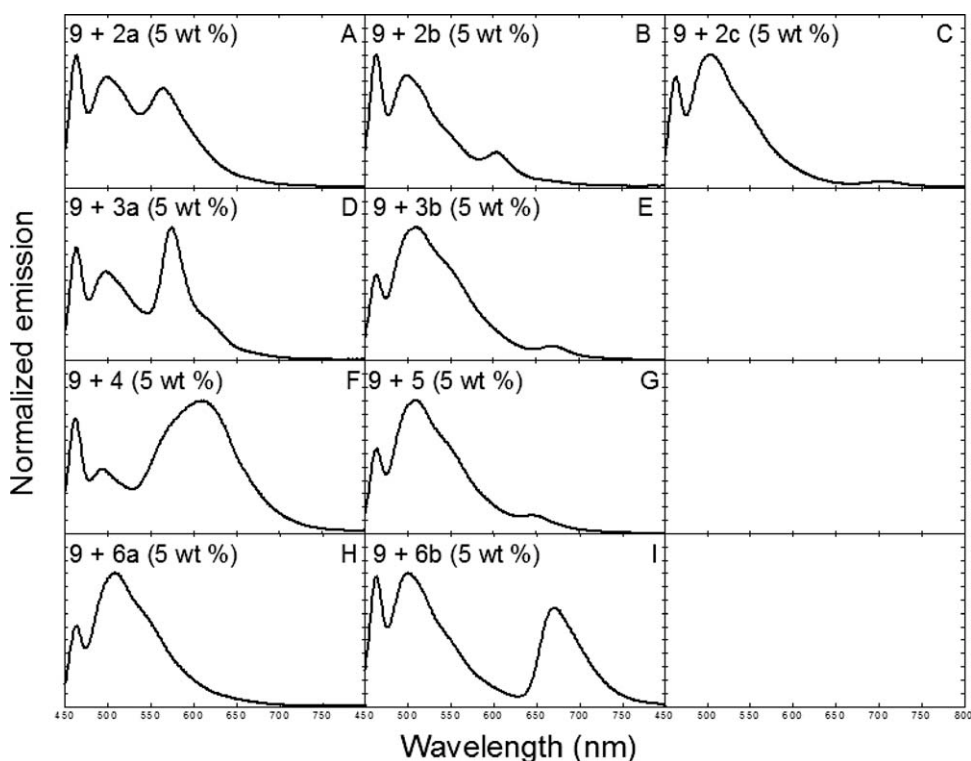


FIGURE 5 Fluorescence spectra of polymer **9**-fluorophore blends in thin films with polymer excitation at 410 nm (solid line). (Y-axis expanded spectra of direct fluorophore excitation are provided in the Supporting Information).

TABLE 5 HOMO and LUMO Levels of Polymer **1** and Fluorophores **2-7** Measured from Their Oxidation (E_{ox}) and Reduction (E_{re}) Potentials, and Their Calculated Band Gaps^a

Compound	HOMO	LUMO	Bandgap (eV)	
	E_{ox} (V) ^b	E_{re} (V) ^b	Electrochemical	Optical
1	-5.74	-3.07 ^c	-	2.67
2a ⁹⁵	-5.66	-3.47	2.19	2.07
2b ⁹⁶	-5.40	-3.30	2.08	1.89
2c	-5.46	-3.86	1.60	1.67
3a	-5.47	-3.31	2.16	2.08
3b	-5.08	-3.53	1.54	1.75
4 ⁹⁷	-5.25	-3.29	1.96	1.98
5	-5.61	-3.97	1.64	1.88
6a ^{98,99}	-5.03	-3.46	1.57	1.85
6b	-5.18	-3.51	1.68	1.82
6c	-5.38 ^c	-3.58	-	1.80
7a ¹⁰⁰	-5.17 ^d	-3.23 ^d	1.75	1.75

^a The CVs of compounds **7b** and **7c** did not provide well-defined oxidation and reduction peaks. Their optical band gaps are similar to the analogous terrylene compound **7a**.

^b Measured versus Fc/Fc⁺.

^c Calculated based on optical band gap.

^d The reference measured potentials versus SCE; they have been converted to potentials versus Fc/Fc⁺.

of polymer **1** are estimated from the oxidation potential and the optical band gaps. Based on the optical bandgap of polymer **1**, and the HOMO-LUMO levels obtained for the fluorophores, it is likely that the HOMO-LUMO energy levels of the acceptors are located between those of the donor polymer. Therefore, all the polymer-fluorophore pairs satisfy the above-mentioned requirements, and are expected to be reasonable candidates for efficient energy transfer without competing PET.

CONCLUSIONS

Highly efficient photoluminescent energy transfer was achieved in polymer-fluorophore blend films with PPE donors and squaraine or terrylene acceptors. The exceptionally high photosensitized emission for compound **6a**, with an increase of two orders of magnitude relative to that obtained by direct fluorophore excitation, suggests that multiple mechanisms of energy transfer may be operative in these systems. Efficient energy transfer depends on a number of factors that influence intrinsic fluorophore emission and the interaction between polymers and fluorophores. The compact and rigid structure of squaraines and their affinity for the polymer allow intimate interaction and orbital overlap. Similarly, the affinity of terrylene compounds **7** for the polymer allows for significant orbital overlap. The internal free volume imparted by the pentipitycene moieties in the host polymer matrix also contributes to competent energy transfer.¹²

Our results offer substantial possibilities for designing turn-on fluorescent sensors. In such sensory schemes, the poly-

mer emission does not overlap the acceptor's emission. Moreover, both squaraines and terrylenes fluoresce in the NIR region, an optimal spectral area for biological imaging.⁴⁷ Thus, the new emission will occur on a completely dark background (free of both polymer emission and interfering biological analytes), leading to even greater sensitivity in the turn-on sensors.

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REFERENCES AND NOTES

- Zheng, J.; Swager, T. M. *Adv Polym Sci* 2005, 177, 151–179.
- Scheblykin, I. G.; Yartsev, A.; Pullerits, T.; Gulbinas, V.; Sundström, V. *J Phys Chem B* 2007, 111, 6303–6321.
- Lai, M.-H.; Chueh, C.-C.; Chen, W.-C.; Wu, J.-L.; Chen, F.-C. *J Polym Sci Part A: Polym Chem* 2009, 47, 973–985.
- Park, J. S.; Ryu, T. I.; Song, M.; Yoon, K.-J.; Lee, M. J.; Shin, I. A.; Lee, G.-D.; Lee, J. W.; Gal, Y.-S.; Jin, S.-H. *J Polym Sci A: Polym Chem* 2008, 46, 6175–6184.
- Morana, M.; Wegscheider, M.; Bonanni, A.; Kopidakis, N.; Shaheen, S.; Scharber, M.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. *Adv Funct Mater* 2008, 18, 1757–1766.
- Xiao, S.; Zhou, H.; You, W. *Macromolecules* 2008, 41, 5688–5696.
- Lv, X.; Mao, J.; Liu, Y.; Huang, Y.; Ma, Y.; Yu, A.; Yin, S.; Chen, Y. *Macromolecules* 2008, 41, 501–503.
- Roncali, J. *Macromol Rapid Commun* 2007, 28, 1761–1775.
- Lu, G.; Tang, H.; Qu, Y.; Li, L.; Yang, X. *Macromolecules* 2007, 40, 6579–6584.
- Colladet, K.; Fourier, S.; Cleij, T. J.; Lutsen, L.; Gelan, J.; Vanderzande, D.; Nguyen, L. H.; Neugebauer, H.; Sariciftci, S.; Aguirre, A.; Janssen, G.; Goovaerts, E. *Macromolecules* 2007, 40, 65–72.
- Moliton, A.; Hiorns, R. C. *Polym Int* 2004, 53, 1397–1412.
- Swager, T. M. *Acc Chem Res* 2008, 41, 1181–1189.
- Ahn, D. J.; Kim, J.-M. *Acc Chem Res* 2008, 41, 805–816.
- Fan, L.-J.; Zhang, Y.; Murphy, C. B., Angell, S. E.; Parker, M. F. L.; Flynn, B. R.; Jones, W. E. *Coord Chem Rev* 2009, 253, 410–422.
- Zhang, L.; Sun, H.; Li, D.; Song, S.; Fan, C.; Wang, S. *Macromol Rapid Commun* 2008, 29, 1489–1494.
- McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem Rev* 2000, 100, 2537–2574.
- Jones, R. M.; Lu, L.; Hegelson, R.; Bergstedt, T. S.; McBranch, D. W.; Whitten, D. G. *Proc Natl Acad Sci USA* 2001, 98, 14769–14772.
- Wang, D.; Gong, X.; Heeger, P. S.; Rininsland, F.; Bazan, G. C.; Heeger, A. J. *Proc Natl Acad Sci USA* 2002, 99, 49–53.
- Stork, M.; Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Adv Mater* 2002, 14, 361–366.

- 20** Zhou, Q.; Swager, T. M. *J Am Chem Soc* 1995, 117, 7017–7018.
- 21** Zhou, Q.; Swager, T. M. *J Am Chem Soc* 1995, 117, 12593–12602.
- 22** Zhao, D.; Swager, T. M. *Macromolecules* 2005, 38, 9377–9384.
- 23** Wosnick, J. H.; Liao, J. H.; Swager, T. M. *Macromolecules* 2005, 38, 9287–9290.
- 24** Joly, G. D.; Geiger, L.; Kooi, S. E.; Swager, T. M. *Macromolecules* 2006, 39, 7175–7177.
- 25** Levitsky, I. A.; Kim, J.; Swager, T. M. *Macromolecules* 2001, 34, 2315–2319.
- 26** Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *Proc Natl Acad Sci USA* 2002, 99, 10954–10957.
- 27** Liu, B.; Bazan, G. C. *Chem Mater* 2004, 16, 4467–4476.
- 28** Ho, H.-A.; Bera-Aberem, M.; Leclerc, M. *Chem Eur J* 2005, 11, 1718–1724.
- 29** Wosnick, J. H.; Mello, C. M.; Swager, T. M. *J Am Chem Soc* 2005, 127, 3400–3405.
- 30** Kumaraswamy, S.; Bergstedt, T.; Shi, X.; Rininsland, F.; Kushon, S.; Xia, W.; Ley, K.; Achyuthan, K.; McBranch, D.; Whitten, D. *Proc Natl Acad Sci USA* 2004, 101, 7511–7515.
- 31** Pinto, M. R.; Schanze, K. S. *Proc Natl Acad Sci USA* 2004, 101, 7505–7510.
- 32** Disney, M. D.; Zheng, J.; Swager, T. M.; Seeberger, P. H. *J Am Chem Soc* 2004, 126, 13343–13346.
- 33** DiCesare, N.; Pinto, M. R.; Schanze, K. S.; Lakowicz, J. R. *Langmuir* 2002, 18, 7785–7787.
- 34** Nilsson, K. P. R.; Olsson, J. D. M.; Stabo-Eeg, F.; Lindgren, M.; Konradsson, P.; Inganaes, O. *Macromolecules* 2005, 38, 6813–6821.
- 35** Feng, F.; He, F.; An, L.; Wang, S.; Li, Y.; Zhu, D. *Adv Mater* 2008, 20, 2959–2964.
- 36** Zhao, D.; Du, J.; Chen, Y.; Ji, X.; He, Z.; Chan, W. *Macromolecules* 2008, 41, 5373–5378.
- 37** Li, J.; Kendig, C. E.; Nesterov, E. E. *J Am Chem Soc* 2007, 129, 15911–15918.
- 38** Ho, H.-A.; Najari, A.; Leclerc, M. *Acc Chem Res* 2008, 41, 168–178.
- 39** Yang, J.-S.; Swager, T. M. *J Am Chem Soc* 1998, 120, 5321–5322.
- 40** Zeng, Q.; Zhang, L.; Li, Z.; Qin, J.; Tang, B. Z. *Polymer* 2009, 50, 434–440.
- 41** Pu, K.-Y.; Liu, B. *Adv Funct Mater* 2009, 19, 277–284.
- 42** Wang, S.; Gaylord, B. S.; Bazan, G. C. *J Am Chem Soc* 2004, 126, 5446–5451.
- 43** Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *J Am Chem Soc* 2003, 125, 896–900.
- 44** Liu, B.; Bazan, G. C. *J Am Chem Soc* 2004, 126, 1942–1943.
- 45** McQuade, D. T.; Hegedus, A. H.; Swager, T. M. *J Am Chem Soc* 2000, 122, 12389–12390.
- 46** Zheng, J.; Swager, T. M. *Chem Commun* 2004, 2798–2799.
- 47** Frangioni, J. V. *Curr Opin Chem Biol* 2003, 7, 626–634.
- 48** Rao, J.; Dragulescu-Andrasi, A.; Yao, H. *Curr Opin Biotechnol* 2007, 18, 17–25.
- 49** Weissleder, R. *Nat Biotechnol* 2001, 19, 316–317.
- 50** Nakayama, A.; del Monte, F.; Hajjar, R. J.; Frangioni, J. V. *Mol Imaging* 2002, 1, 365–377.
- 51** Sakatani, K.; Kashiwasake-Jibu, M.; Taka, Y.; Wang, S.; Zuo, H.; Yamamoto, K.; Shimizu, K. *J Neurosurg* 1997, 87, 738–745.
- 52** Weissleder, R.; Tung, C.-H.; Mahmood, U.; Bogdanov, A., Jr. *Nat Biotechnol* 1999, 17, 375–378.
- 53** Chen, J.; Tung, C.-H.; Mahmood, U.; Ntziachristos, V.; Gyurko, R.; Fishman, M. C.; Huang, P. L.; Weissleder, R. *Circulation* 2002, 105, 2766–2771.
- 54** Nesterov, E. E.; Skoch, J.; Hyman, B. T.; Klunk, W. E.; Bacskaï, B. J.; Swager, T. M. *Angew Chem Int Ed* 2005, 44, 5452–5456.
- 55** Hintersteiner, M.; Enz, A.; Frey, P.; Jatón, A.; Kinzy, W.; Kneuer, R.; Neumann, U.; Rudin, M.; Staufienbiel, M.; Stoeckli, M.; Wiederhold, K.; Gremlich, H. *Nat Biotechnol* 2005, 23, 577–583.
- 56** Yang, J.-S.; Swager, T. M. *J Am Chem Soc* 1998, 120, 11864–11873.
- 57** Kim, J.; Swager, T. M. *Nature* 2001, 411, 1030–1034.
- 58** Block, M. A. B.; Hecht, S. *Macromolecules* 2004, 37, 4761–4769.
- 59** Snee, P. T.; Somers, R. C.; Nair, G.; Zimmer, J. P.; Bawendi, M. G.; Nocera, D. G. *J Am Chem Soc* 2006, 128, 13320–13321.
- 60** Isgor, Y. G.; Akkaya, E. U. *Tetrahedron Lett* 1997, 38, 7417–7420.
- 61** Holtrup, F. O.; Müller, G. R. J.; Quante, H.; De Feyter, S.; De Schryver, F. C.; Müllen, K. *Chem Eur J* 1997, 3, 219–225.
- 62** Nolde, F.; Qu, J.; Kohl, C.; Pschirer, N. G.; Reuther, E.; Müllen, K. *Chem Eur J* 2005, 11, 3959–3967.
- 63** Sreejith, S.; Carol, P.; Chithra, P.; Ajayaghosh, A. *J Mater Chem* 2008, 18, 264–274.
- 64** Ajayaghosh, A. *Acc Chem Res* 2005, 38, 449–459.
- 65** Basheer, M. C.; Alex, S.; George Thomas, K.; Suresh, C. H.; Das, S. *Tetrahedron* 2006, 62, 605–610.
- 66** Arunkumar, E.; Ajayaghosh, A.; Daub, J. *J Am Chem Soc* 2005, 127, 3156–3164.
- 67** Oguz, U.; Akkaya, E. U. *Tetrahedron Lett* 1998, 39, 5857–5860.
- 68** Akkaya, E. U.; Turkyilmaz, S. *Tetrahedron Lett* 1997, 38, 4513–4516.
- 69** Ros-Lis, J. V.; Garcia, B.; Jimenez, D.; Martinez-Manez, R.; Sancenón, F.; Soto, J.; Gonzalvo, F.; Valldecabres, M. C. *J Am Chem Soc* 2004, 126, 4064–4065.
- 70** Ioffe, V. M.; Gorbenko, G. P.; Domanov, Y. A.; Tatarets, A. L.; Patsenker, L. D.; Terpetching, E. A.; Dyubko, T. S. *J Fluoresc* 2006, 16, 47–52.

- 71** Gassensmith, J. J.; Barr, L.; Baumes, J. M.; Paek, A.; Nguyen, A.; Smith, B. D. *Org Lett* 2008, 10, 3343–3346.
- 72** Arunkumar, E.; Fu, N.; Smith, B. D. *Chem Eur J* 2006, 12, 4684–4690.
- 73** Arunkumar, E.; Forbes, C. C.; Noll, B. C.; Smith, B. D. *J Am Chem Soc* 2005, 127, 3288–3289.
- 74** Umezawa, K.; Citterio, D.; Suzuki, K. *Anal Sci* 2008, 24, 213–217.
- 75** Gassensmith, J. J.; Arunkumar, E.; Barr, L.; Baumes, J. M.; DiVittorio, K. M.; Johnson, J. R.; Noll, B. C.; Smith, B. D. *J Am Chem Soc* 2007, 129, 15054–15059.
- 76** Clar, E.; Speakman, J. C. *J. Chem Soc* 1958, 2492–2494.
- 77** Clar, E.; Müllen, A. *Tetrahedron* 1971, 27, 5239–5245.
- 78** Adachi, M.; Nagao, Y. *Chem Mater* 2001, 13, 662–669.
- 79** Rodriguez-Hernandez, J.; Qu, J.; Reuther, E.; Klok, H.-A.; Müllen, K. *Poly Bull* 2004, 52, 57–64.
- 80** Weil, T.; Abdalla, M. A.; Jatzke, C.; Hengstler, J.; Müllen, K. *Biomacromolecules* 2005, 6, 68–79.
- 81** Jung, C.; Müller, B. K.; Lamb, D. C.; Nolde, F.; Müllen, K.; Braeuchle, C. *J Am Chem Soc* 2006, 128, 5283–5291.
- 82** Peneva, K.; Mihov, G.; Nolde, F.; Rocha, S.; Hotta, J.; Braeckmans, K.; Hofkens, J.; Uji-i, H.; Herrmann, A.; Müllen, K. *Angew Chem Int Ed* 2008, 47, 3372–3375.
- 83** Förster, T. *Discuss Faraday Soc* 1959, 27, 7–17.
- 84** Johnson, J. R.; Fu, N.; Arunkumar, E.; Leevy, W. M.; Gammon, S. T.; Piwnica-Worms, D.; Smith, B. D. *Angew Chem Int Ed* 2007, 46, 5528–5531.
- 85** Chen, H.; Herkstroeter, W. G.; Perlstein, J.; Law, K.-Y.; Whitten, D. G. *J Phys Chem* 1994, 98, 5138–5146.
- 86** Xue, M.; Chen, C.-F. *Chem Commun* 2008, 6128–6130.
- 87** Liu, B.; Bazan, G. C. *J Am Chem Soc* 2006, 128, 1188–1196.
- 88** Guldi, D. M.; Swartz, A.; Luo, C.; Gómez, R.; Segura, J. L.; Martín, N. *J Am Chem Soc* 2002, 124, 10875–10886.
- 89** Halls, J. J. M.; Cornil, J.; dos Santos, D. A.; Silbey, R.; Hwang, D.-H.; Holmes, A. B.; Brédas, J. L.; Friend, R. H. *Phys Rev B* 1999, 60, 5721–5727.
- 90** Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* 1992, 258, 1474–1476.
- 91** Xu, Q.-H.; Moses, D.; Heeger, A. J. *Phys Rev B* 2003, 67, 245417/1–245417/5.
- 92** Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem Rev* 2004, 104, 4971–5003.
- 93** Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Baessler, H.; Porsch, M.; Daub, J. *Adv Mater* 1995, 7, 551–554.
- 94** Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem Mater* 2004, 16, 2165–2169.
- 95** Gould, I. R.; Shukla, D.; Giesen, D.; Farid, S. *Helv Chim Acta* 2001, 84, 2796–2812.
- 96** Torimura, M.; Kurata, S.; Yamada, K.; Yokomaku, T.; Kamagata, Y.; Kanagawa, T.; Kurane, R. *Anal Sci* 2001, 17, 155–160.
- 97** Pugliese, T.; Godbert, N.; Aiello, I.; La Deda, M.; Ghedini, M.; Amati, M.; Belviso, S.; Lelj, F. *Dalton Trans* 2008, 6563–6572.
- 98** Liang, K.; Law, K.-Y.; Whitten, D. G. *J Phys Chem B* 1997, 101, 540–546.
- 99** Piechowski, A. P.; Bird, G. R.; Morel, D. L.; Stogryn, E. L. *J Phys Chem* 1984, 88, 934–950.
- 100** Lee, S. K.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. *J Am Chem Soc* 1999, 121, 3513–3520.