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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 pentiptycene-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

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and the enhancement of the fluorophore emission. Near-infrared emitting squaraines and terrylenes 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.

Introduction

The highly efficient energy transfer[1] and exciton migration processes[2] 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

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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 nm 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 diisopropylamine were purchased from Aldrich

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Chemical Company, Inc 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 Probes[TM]. 1,1'-Diethyl-3,3,3',3'-tetramethylindocarbocyanine 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-dihydroxycyclobutenediylium dihydroxide (**6a**) and 1,3-bis[4-[bis(2-methylpropyl)amino]-2,6-dihydroxyphenyl]-2,4-dihydroxy cyclobutenediylium (**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]

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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, etc.) and these polymers are therefore utilized interchangeably. The fact that the results described in this paper are not dependent upon the minor spatial perturbations that will exist between these polymers is evidence for the robustness of our conclusions.

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**. Squaraines 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]

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}) x 10^4

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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 synthesis of terrylenediimide fluorophores **7** is shown in **Scheme 1**. Terrylene, which

was first crystallized by Clar in 1958,[76] demonstrates a substantial bathochromic 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]

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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, *i.e.* 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 the fractional quenching of donor emission (E_{exp}) as in Equation 1:

$$E_{exp} = 1 - F_{DA}/F_D$$

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 weight % and 0.5 weight % (**Table 2**). For some of the more interesting NIR acceptors, we examined films with extended compositional ranges (**Table 3**).

Table 2

Energy transfer efficiencies measured by the decrease in polymer emission (E_{exp}) and the increase of fluorophore emission (I_{AD}/I_A) in thin films of polymer **1** with the fluorophores at 0.5 wt % and 5 wt % doping concentration

Fluorophore	5 wt %		0.5 wt %	
	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_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.

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Table 3

Energy transfer efficiencies measured by the decrease in polymer emission (E_{exp}) and the increase of fluorophore emission (I_{AD}/I_A) in thin films of polymer **1** with fluorophores **6c-7c** at various concentrations

	1 wt %		0.1 wt %	
Fluorophore	**E_{exp}**	**I_{AD}/I_A**	**E_{exp}**	**I_{AD}/I_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.

The fluorophore emission observed for rhodamine compounds **2** decreases as the absorption maximum of the compounds increases (**Figure 2A-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.

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The cyanine compounds **3** show reduced sensitized fluorophore emissions, especially for compound **3b** (**Figure 2D-E**). Although thin films with Nile Red **4** show efficient energy transfer (**Figure 2F**), its cationic analogue oxazine **5** does not function as an efficient energy acceptor (**Figure 2G**). 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 70-fold increase in the fluorophore emission (I_{AD}/I_A) for compounds **6a** and **6b**, respectively (**Figure 2H-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 polymer excitation, with up to a 54-fold increase in the fluorophore's emission (**Figure 2J**). 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** (**Figure 2K-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

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neither 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 rigid and compact size of 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

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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).

When compared to polymer **1**, polymer **9** shows less efficient energy transfer in terms of both donor quenching and amplified acceptor emission (**Table 4**, **Figure 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 in the spin-casting process and facilitates the entrapment of the fluorophores in close proximity to the polymer backbone.

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_{AD}/I_A)

	5 wt %		0.5 wt%	
	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_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.

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 non-radiative

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relaxation.[90-92] Therefore, the HOMO-LUMO energy levels of the donor should bracket those of the acceptor to minimize the non-radiative 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 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.

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.[d]

	HOMO	LUMO	bandgap (eV)	
compound	E_{ox} (V)[a]	E_{re} (V)[a]	electrochemical	optical
1	-5.74	-3.07[b]	-	2.67
2a[95]	-5.66	-3.47	2.19	2.07
2b[96]	-5.40	-3.30	2.08	1.89

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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[b]	-3.58	-	1.80
7a[100]	-5.17[c]	-3.23[c]	1.75	1.75

[a] Measured vs. Fc/Fc^+.

[b] Calculated based on optical band gap.

[c] The reference measured potentials vs. SCE; they have been converted to potentials vs. Fc/Fc^+.

[d] 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**.

Conclusion

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

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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 pentiptycene 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 polymer 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.

Acknowledgements

Supplementary Information

Details of spectroscopic and thin film experiments, Y-axis expanded spectra of direct fluorophore excitations, qualitative mechanistic calculations, spectra of fluorophores with

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polymers at various concentrations, lifetimes of polymers and fluorophores in thin films. This material is available free of charge.

Figure Legends

Figure 1

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

Figure 2

Fluorescence spectra of polymer-fluorophore blends in thin films with polymer excitation at 410 nm (solid line). (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.

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, Φ_F = 0.04, n (633 nm) = 1.57; chloroform solution: λ_{max} abs. = 413 nm, λ_{max} em. = 447 nm, Φ_F = 0.41).

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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).

Scheme 1

Synthesis of terrylene fluorophores **7**

Chart 1

Organic fluorophores used in the energy transfer studies.

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Graphical Abstract

Blended thin films were fabricated which contain conjugated fluorescent polymers and near-infrared emitting fluorophores. Highly efficient energy transfer was observed from the polymer to the fluorophore, with nearly two orders of magnitude amplified fluorophore emission observed in the near-infrared spectral region. This amplified emission does not require appreciable spectral overlap between the polymer emission and fluorophore absorption spectra. Our results offer substantial possibilities in the design of highly sensitive turn-on fluorescent sensors with negligible background polymer emission in the spectral region of interest.
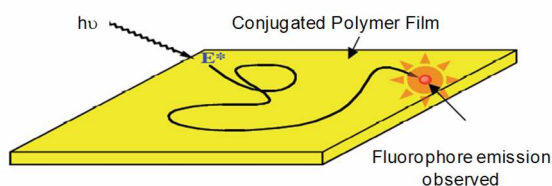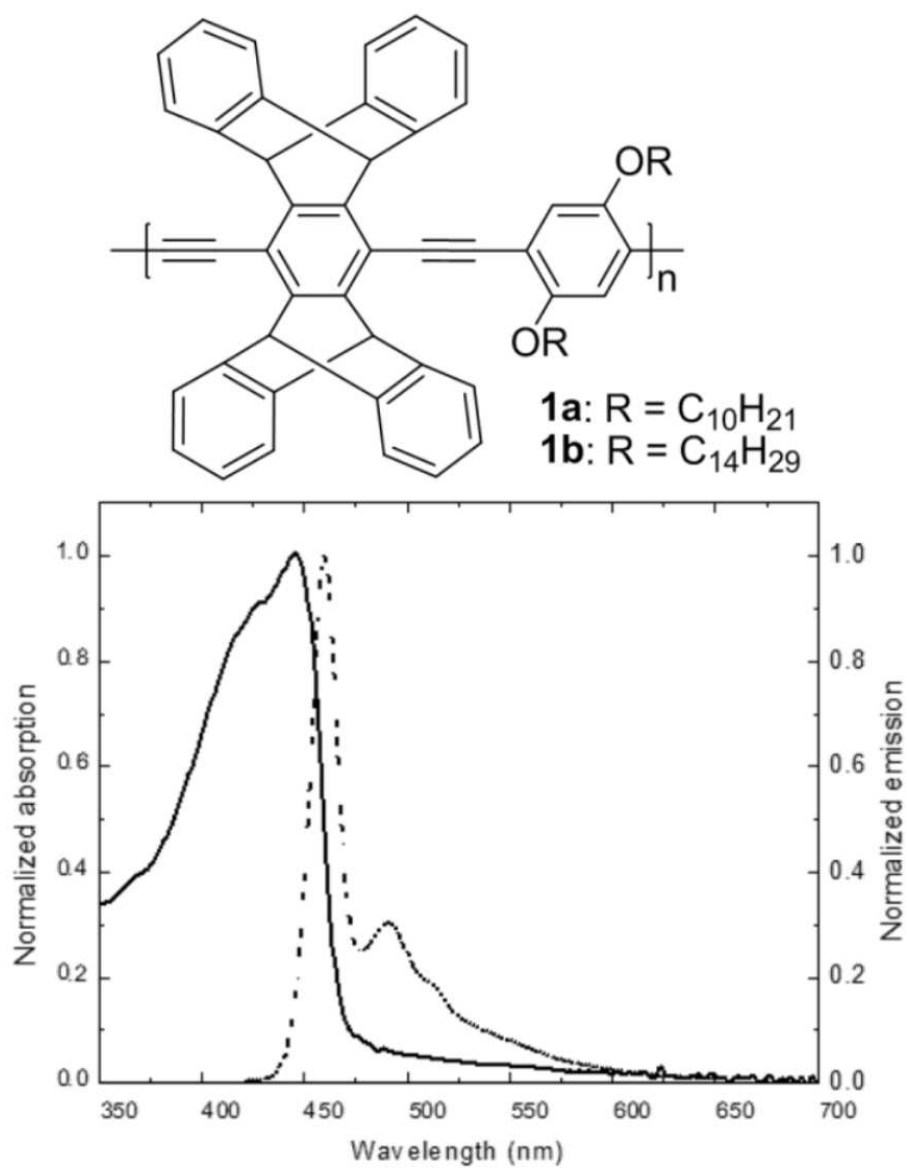
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Figure 1. The absorption (solid line) and emission (dashed line) spectra of polymer 1a in spin-cast films (Thin films: λmax abs. = 446 nm, λmax em. = 460 nm, ΦF = 0.33, n (633 nm) = 1.66; chloroform solution: λmax abs. = 427 nm, λmax em. = 453 nm, ΦF = 0.50).
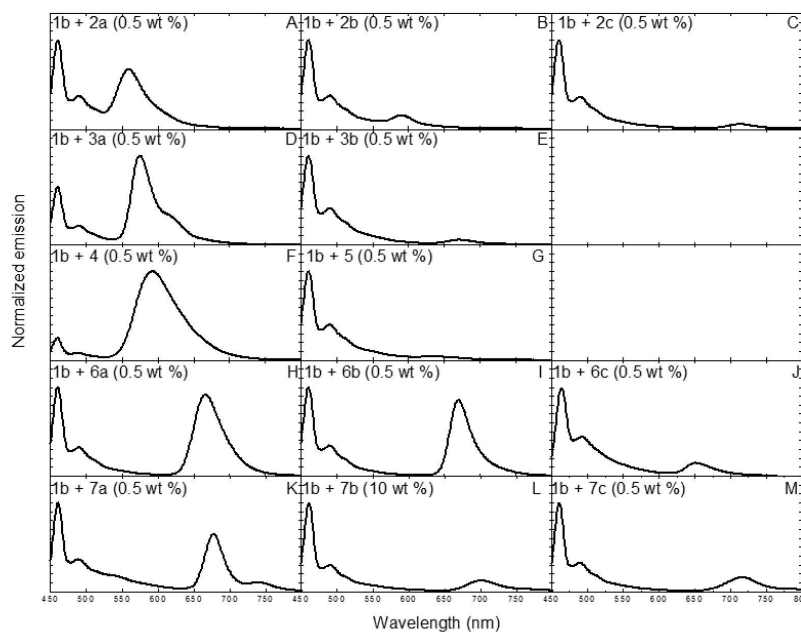77x97mm (300 x 300 DPI)

Figure 2. Fluorescence spectra of polymer-fluorophore blends in thin films with polymer excitation at 410 nm (solid line). (Y-axis expanded spectra of direct excitation of fluorophores is provided in the Supporting Information).
165x126mm (600 x 600 DPI)
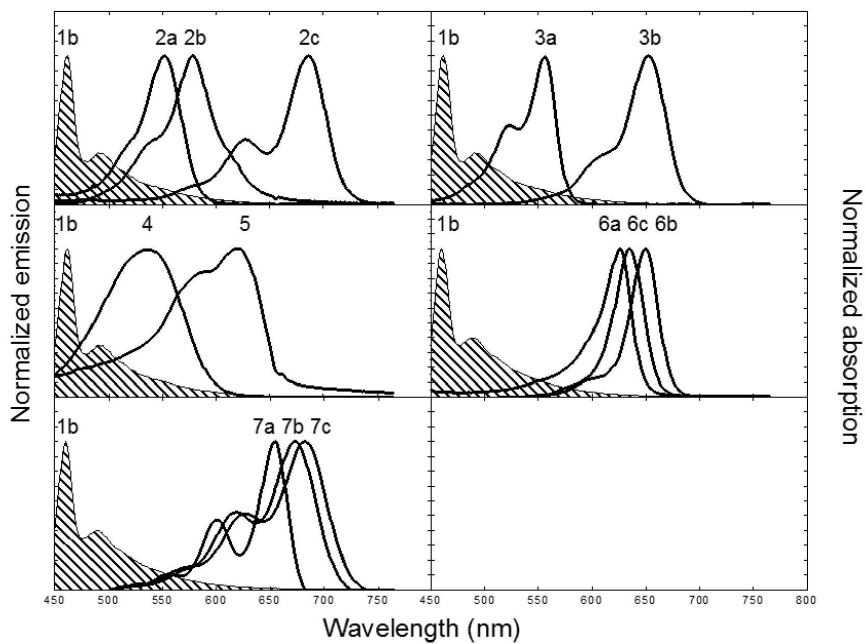
Figure 3. Overlaid spectra of the emission of polymer 1 with the absorbance of the fluorophores.
The hatched area represents the emission band of the pristine polymer.
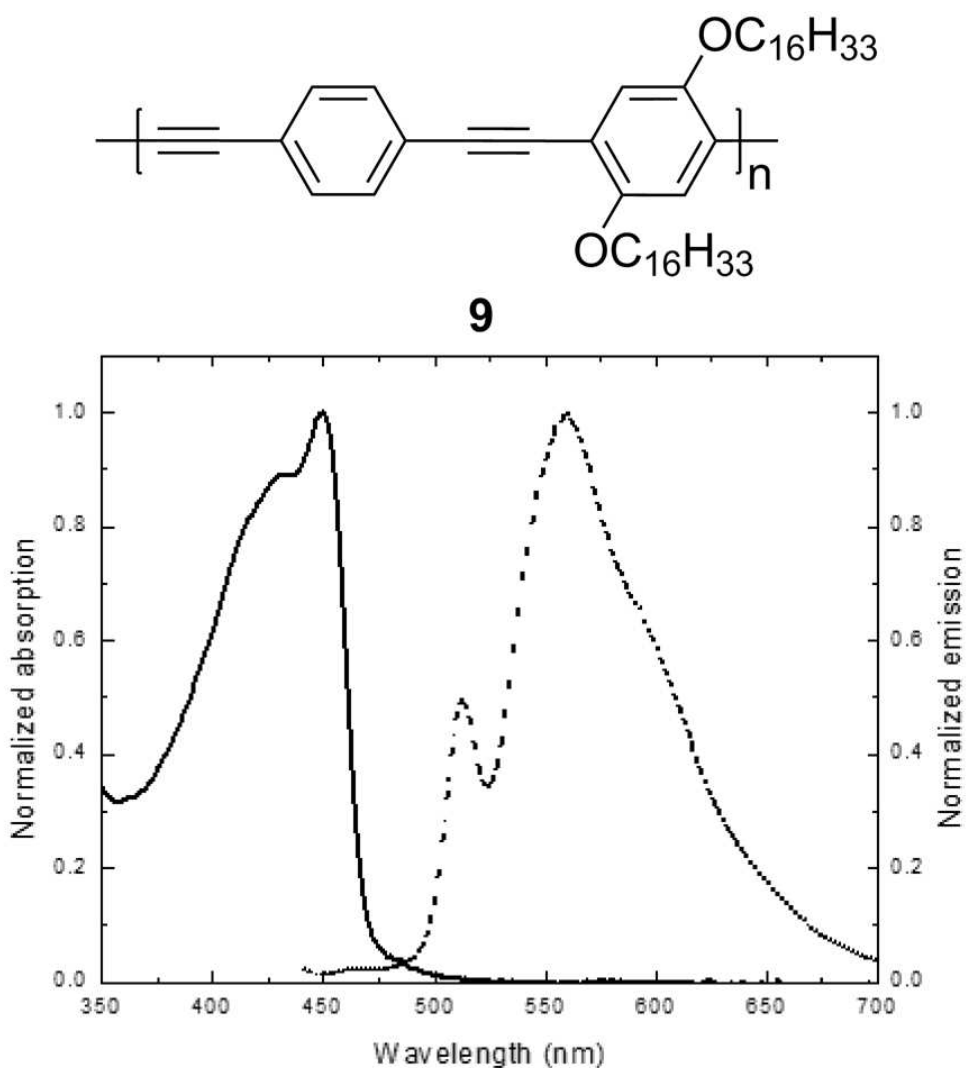165x126mm (600 x 600 DPI)

Figure 4. The absorption (solid line) and emission (dashed line) spectra of polymer 9 in spin-cast films (Thin films: λmax abs. = 449 nm, λmax em. = 463 nm, 511 nm, ΦF = 0.04, n (633 nm) = 1.57; chloroform solution: λmax abs. = 413 nm, λmax em. = 447 nm, ΦF = 0.41).
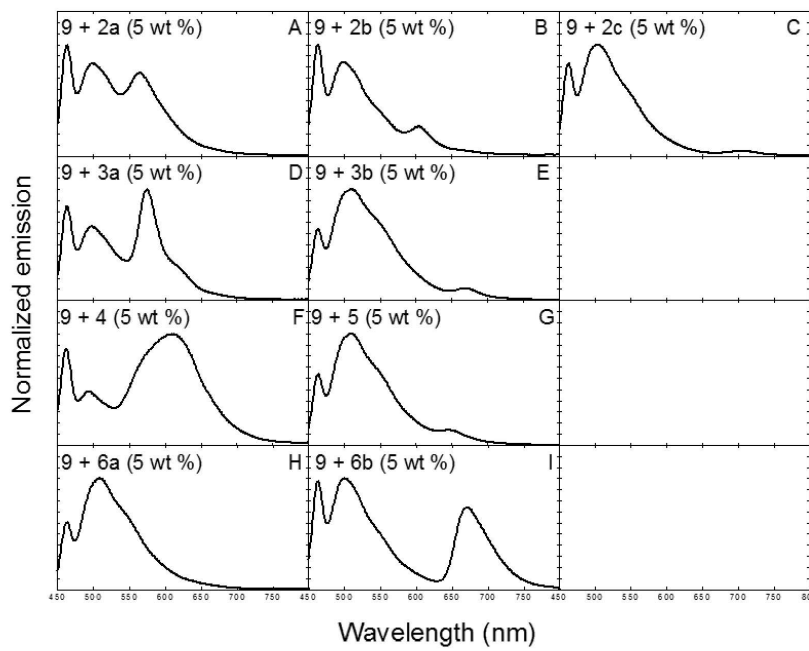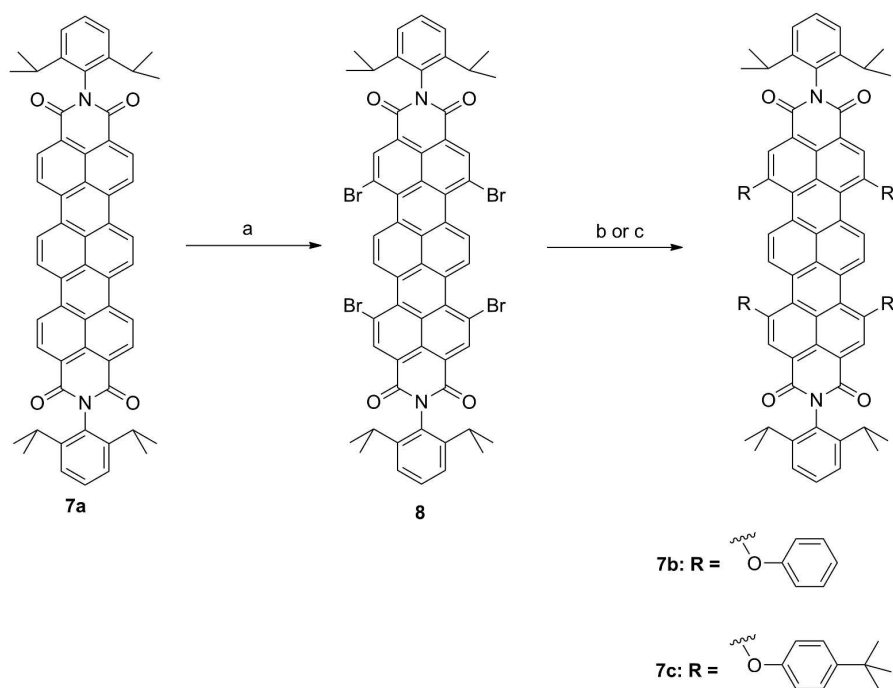75x82mm (300 x 300 DPI)

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).
165x126mm (600 x 600 DPI)

7b: R =

7c: R =

(a) Br$_2$, CHCl$_3$, 100°C, 75% yield; (b) **7b**: phenol, K$_2$CO$_3$, N-methyl pyrrolidone (NMP), 80°C, 90% yield; (c) **7c**: *t*-butyl phenol, K$_2$CO$_3$, NMP, 80°C, 86% yield

Scheme 1. Synthesis of terrylene fluorophores 7
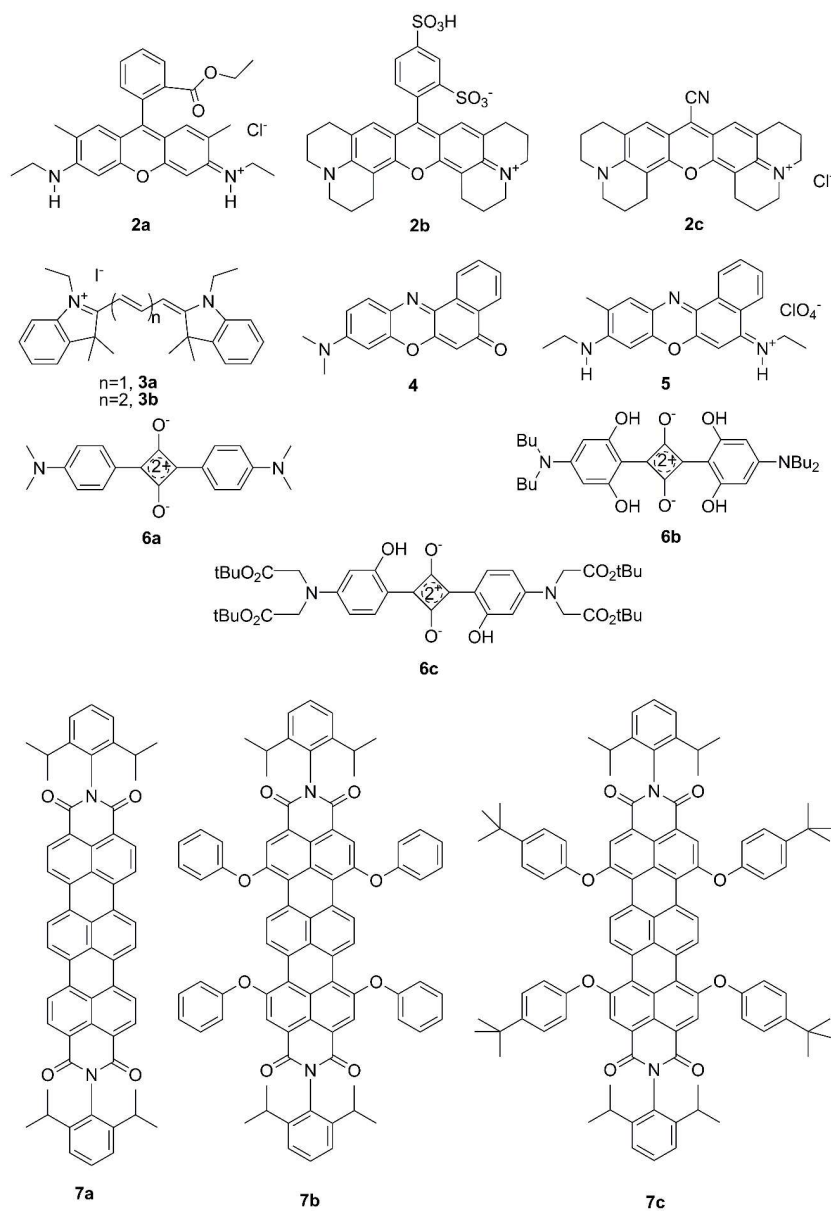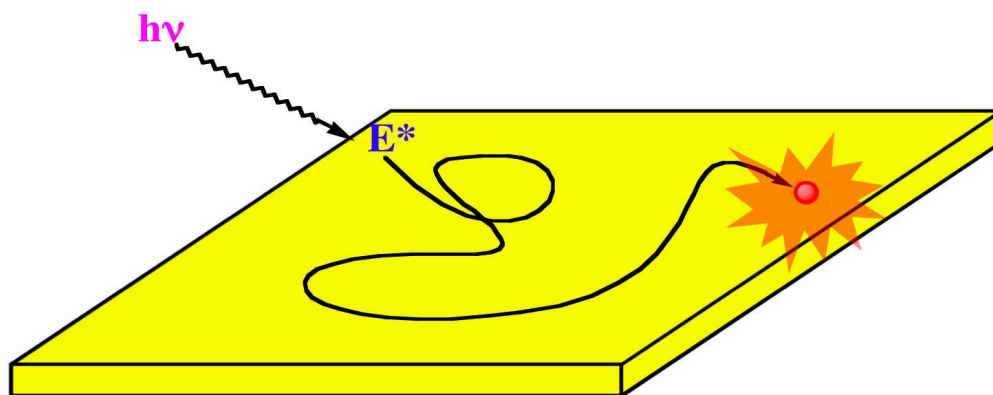147x110mm (600 x 600 DPI)

Chart 1. Organic fluorophores used in the energy transfer studies.
166x240mm (600 x 600 DPI)

Exciton Diffusion to an Emissive Trap
513x201mm (72 x 72 DPI)

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}) x 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.

Table 2

Energy transfer efficiencies measured by the decrease in polymer emission (E_{exp}) and the increase of fluorophore emission (I_{AD}/I_A) in thin films of polymer **1** with the fluorophores at 0.5 wt % and 5 wt % doping concentration

Fluorophore	5 wt %		0.5 wt %	
	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_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.

^b Polymer emission is not quenched at this concentration.

Table 3

Energy transfer efficiencies measured by the decrease in polymer emission (E_{exp}) and the increase of fluorophore emission (I_{AD}/I_A) in thin films of polymer **1** with fluorophores **6c-7c** at various concentrations

	1 wt %		0.1 wt %	
Fluorophore	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_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.

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_{AD}/I_A)

	5 wt %		0.5 wt%	
	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_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.

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.[d]

	HOMO	LUMO	bandgap (eV)	
compound	E_{ox} (V)[a]	E_{re} (V)[a]	electrochemical	optical
1	-5.74	-3.07[b]	-	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[b]	-3.58	-	1.80
7a[100]	-5.17[c]	-3.23[c]	1.75	1.75

[a] Measured vs. Fc/Fc[+].

[b] Calculated based on optical band gap.

[c] The reference measured potentials vs. SCE; they have been converted to potentials vs. Fc/Fc[+].

[d] 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**.

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- S1 -

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

Supporting Information

Mindy Levine, Inja Song, Trisha L. Andrew, Steven E. Kooi, Timothy M. Swager*

- S2 -

Table of Contents

Thin film experiments:

The thin films used in these experiments were fabricated from chloroform solutions. Stock solutions of 1.0 mg/mL of polymers **1a** and **1b**, and 0.5 mg/mL of polymer **9** in chloroform were mixed with the corresponding amount of fluorophore stock solutions. The films were spin-cast at a spin rate of 1000 rpm from chloroform solutions on glass substrates for 1 minute. UV-Vis spectra were obtained on an Agilent 8453 UV-visible spectrophotometer. Fluorescence spectra were measured on a SPEX Fluorolog-τ3 fluorimeter (model FL-321, 450 W Xenon lamp). Polymer thin film spectra were recorded by front-face detection. The slit widths on the fluorimeter were 3 nm excitation slit width and 5 nm emission slit width.

Fluorescence quantum yields of the polymers in chloroform were determined relative to solutions of quinine sulfate (~10^{-6} M in 0.1 N sulfuric acid) ($\Phi_F = 0.55$).[1] The solid state quantum yields were obtained relative to 1 weight % 9,10-diphenylanthracene in poly(methyl methacrylate) (PMMA) ($\Phi_F = 0.83$) as a standard.[2]

To determine the fractional quenching of the polymer's emission in the presence of the acceptor fluorophores, at least six individual measurements of pristine polymer thin films (made from 0.5-1.5 mg/mL of polymer solutions in chloroform) were used to derive a linear relationship between the integrated emission of the polymer and its optical density at the excitation wavelength. The standard curve of the integrated fluorescence intensity versus the corresponding optical density values was obtained by excitation of the pristine polymer thin films at 370 nm for polymers **1a** and **9**. Thin films of polymer **1b** were excited at 410 nm. The integrated donor emission in polymer-fluorophore blended films was obtained under the same conditions, and its corresponding unquenched integrated polymer emission was then derived from the standard curve versus the absorption of the blend film. These values were used for the calculation of donor quenching.

The amplification of fluorophore emission was determined from the ratio of integrated emission of fluorophore with excitation of polymer (I_{AD}) at 410 nm to that obtained upon direct excitation of the fluorophore (I_A). I_{AD} was obtained after deconvolution of any overlapping polymer emission. Direct excitation of fluorophores to obtain I_A is ideally measured by the excitaiton at the fluorophore's absorption maximum to get the highest emission intensity. However, due to the small Stokes shifts of the fluorophores, excitation at the absorption maximum of fluorophores does not yield the complete fluorophore emission spectra. Therefore, we excited the fluorophores at the 30 nm blue-shifted absorption maximum (λ_{max} abs. of fluorophore – 30 nm). For this reason, I_{AD}/I_A is larger than it would be if we excited the fluorophore at its absorption maximum.

We examined the direct excitation of fluorophores **6c** and **7a** (one example of each class of near-infrared emitting fluorophores) at three different wavelengths: the absorption maximum of the fluorophore in thin films with polymer **1**, 15 nm less than the absorption maximum, and 30 nm less than the absorption maximum. In all cases, we observed a substantial amplification of fluorophore emission from exciting the polymer at 410 nm compared to exciting the fluorophore directly (at any of the three wavelengths).

For squaraine compound **6c**, exciting blended thin films with 5 weight % fluorophore at 604 nm (30 nm blue-shifted, 43-fold amplification) resulted in a slightly increased amplification compared to exciting the fluorophore at 619 nm (15 nm blue-shifted, 36-fold amplification). When the same film was excited directly at the absorption maximum of fluorophore **6c** (634 nm), the observed amplification (I_{AD}/I_A) decreased to 29. This decreased amplification is expected based on the increased optical density of the fluorophore at wavelengths close to its absorption maximum.

For terrylene compound **7a**, we observe decreased amplification at most concentrations from exciting the fluorophore at 654 nm (15 nm blue-shifted from the absorption maximum) compared to exciting it at 639 nm (30 nm blue-shifted) (Table S1). Exciting the fluorophore directly at its absorption maximum (669 nm) resulted in truncating too much of the fluorophore emission spectrum.

Table S1: I_{AD}/I_A of thin films of polymer **1** and fluorophore **7a**

Fluorophore concentration	I_{AD}/I_A (639 nm excitation)	I_{AD}/I_A (654 nm excitation)
25 weight %	3.8	4.0
10 weight %	11.8	9.8
5 weight %	23.3	16.5
1 weight %	31.0	24.2
0.5 weight %	48.8	36.3
0.1 weight %	24.0	25.5

For both of the near-infrared emitting fluorophores that we investigated, good to excellent amplification of the fluorophore's emission was still observed, even at the lower I_{AD}/I_A values that were obtained from excitation of the fluorophore at or closer to the absorption maximum.

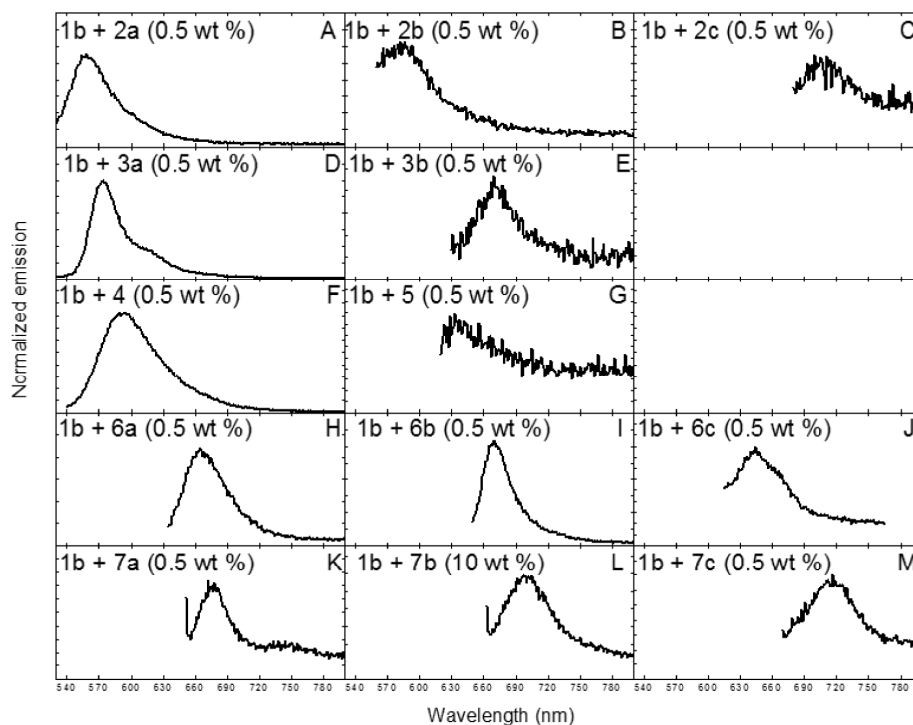*Y-axis expanded spectra of polymer **1** and polymer **9** in thin films with fluorophores:*

Figure S1: Y-axis expanded fluorescence spectra of polymer **1**-fluorophore blends in thin films with direct excitation of the fluorophores.
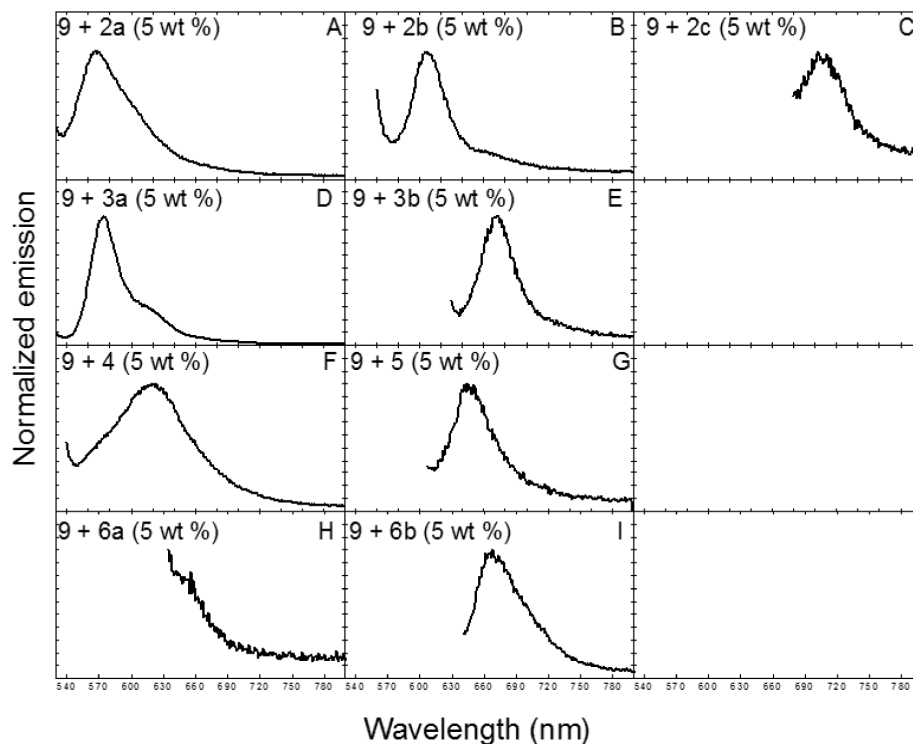

Figure S2: Y-axis expanded fluorescence spectra of polymer **9**-fluorophore blends in thin films with direct excitation of the fluorophores.

Qualitative mechanistic calculations:

If dipolar coupling (Förster energy transfer) is the predominant mechanism of energy transfer, then the rate of energy transfer should be directly proportional to the spectral overlap between the polymer's emission spectrum and the fluorophore's absorption spectrum. We calculated the spectral overlap using PhotoChemCAD for all fluorophores and the results are summarized in Table S2.

Table S2: Spectral overlap integrals (*J*) of fluorophores with polymer **1**

Fluorophore	J ($\text{Å}^6\text{mol}^{-1}$)
2a	1.1×10^{35}
2b	5.4×10^{34}
2c	2.2×10^{34}
3a	1.7×10^{35}
3b	5.0×10^{34}
4	1.3×10^{35}
5	4.6×10^{34}
6a	1.8×10^{34}
6b	3.9×10^{34}
6c	1.5×10^{34}
7a	8.9×10^{33}
7b	5.9×10^{33}
7c	1.4×10^{34}

The ratio of the fluorophore's emission from polymer excitation divided by the spectral overlap integral J was calculated for all fluorophores and is summarized in Table S3. These non-rigorous calculations support the qualitative conclusion that the energy transfer from polymer **1** to small-molecule fluorophores is particularly efficient for near-infrared emitting squaraines and terrylenes (as evidenced by the large values of fluorophore emission divided by the spectral overlap integral observed for these fluorophores), beyond what would be expected based on Förster theory alone.

Table S3: Fluorophore emission intensity divided by spectral overlap integral J

Fluorophore	Polymer 1
2a	0.095
2b	0.038
2c	0.019
3a	0.076
3b	0.012
4	0.15
5	0.011
6a	0.51
6b	0.17
6c	0.24
7a	0.25
7b	1.00
7c	0.24

The same calculations were performed for polymer **9** and the results are summarized in Tables S4 and S5. In the case of polymer **9**, substantially different ratios of fluorophore emission divided by the spectral overlap integral indicate that non-Förster energy transfer mechanisms are likely operative in these systems.

Table S4: Spectral overlap integrals (J) and Forster radii (R_o) of fluorophores with polymer **9**

Fluorophore	J ($Å^6 mol^{-1}$)[a]
2a	3.4×10^{35}
2b	3.2×10^{35}
2c	1.2×10^{35}
3a	4.8×10^{35}
3b	4.5×10^{35}
4	2.4×10^{35}
5	2.0×10^{35}
6a	2.1×10^{35}
6b	3.7×10^{35}

Table S5: Fluorophore emission intensity divided by spectral overlap integral J

Fluorophore	Polymer 9
2a	0.38
2b	0.080
2c	0.046
3a	0.33
3b	0.017
4	1.00
5	0.032
6b	0.23

High fluorophore concentrations:

Thin films were fabricated at 100 weight %, 50 weight %, 25 weight %, and 10 weight % of fluorophores **6c-7c** in polymer **1** (Table S6). While multiple complicated processes may be occuring in these films, we nonetheless observe some amplification of the fluorophore emission, as well as excellent to moderate quenching of the polymer's emission.

Table S6: Energy transfer efficiencies measured by the decrease in polymer emission (E_{exp}) and the increase of fluorophore emission (I_{AD}/I_A) in thin films of polymer **1** with the fluorophores at high fluorophore concentrations:

Fluorophore	100 wt %		50 wt %		25 wt %		10 wt %	
	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_A	E_{exp}	I_{AD}/I_A
6c	0.87	18.7	0.87	12.1	0.67	29.4	0.43	49.0
7a	0.97	*a*	0.97	4.2	0.95	7.3	0.92	10.9
7b	0.67	5.3	0.46	9.3	0.11	19.7	*b*	38.0
7c	0.96	1.6	0.93	2.6	0.85	4.9	0.72	11.3

[a] Fluorophore is not emissive at this concentration

[b] Polymer emission is not quenched at this concentration

*All spectra of fluorophores **6c-7c** in thin films with polymer **1b** at various concentrations:* The emission from exciting polymer **1b** is represented by the solid line. Y-axis expanded spectra of direct fluorophore excitation are provided in subsequent figures.
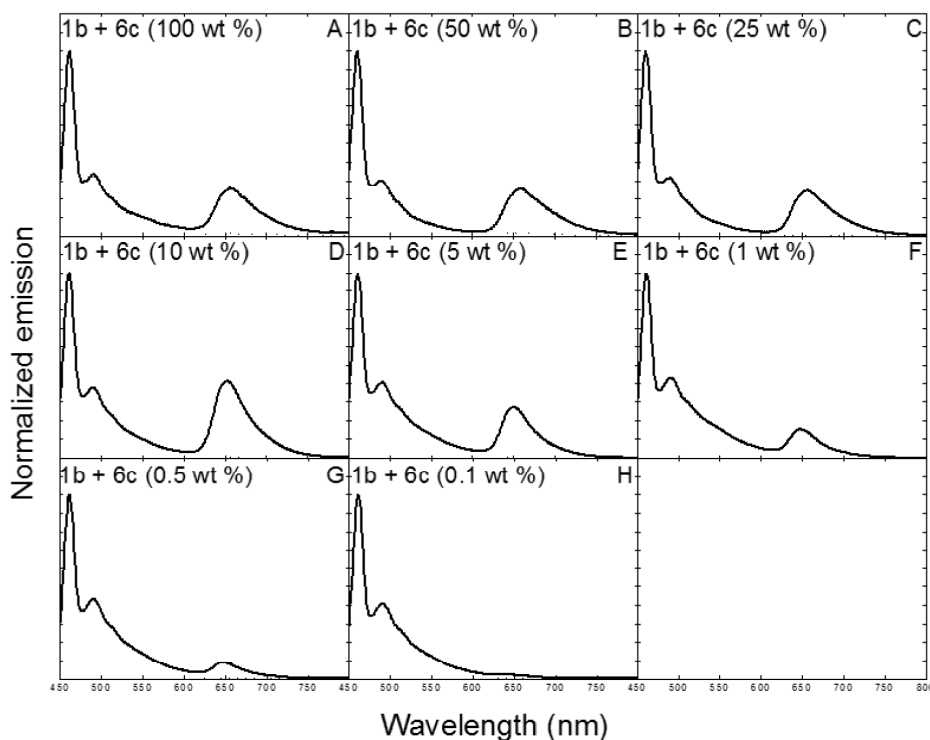

Figure S3: Thin films of polymer **1b** and fluorophore **6c** at various fluorophore concentrations.
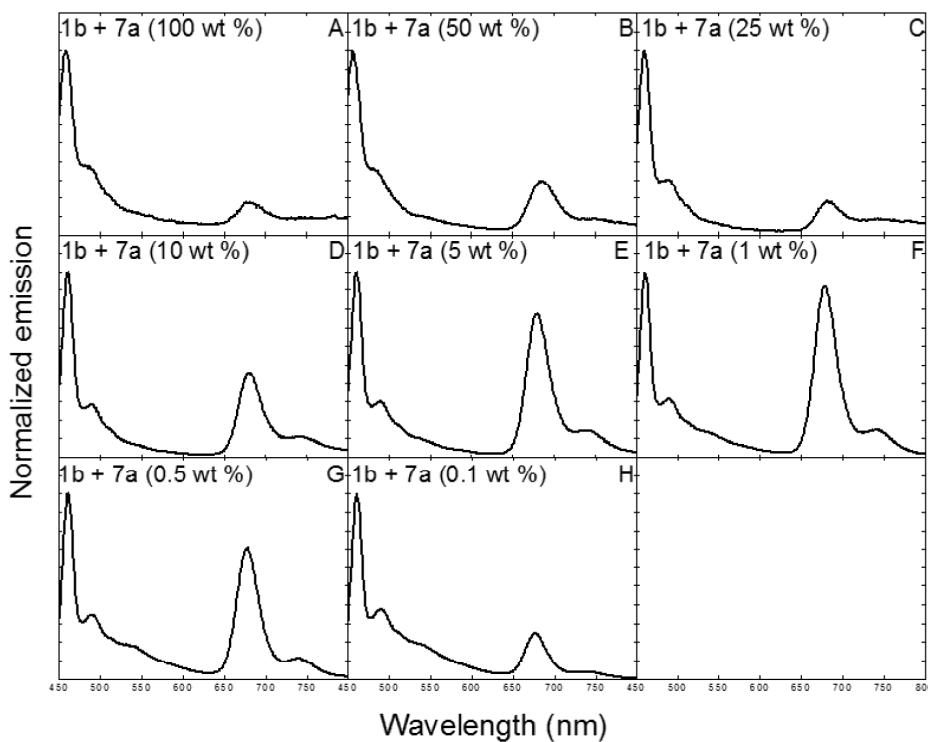

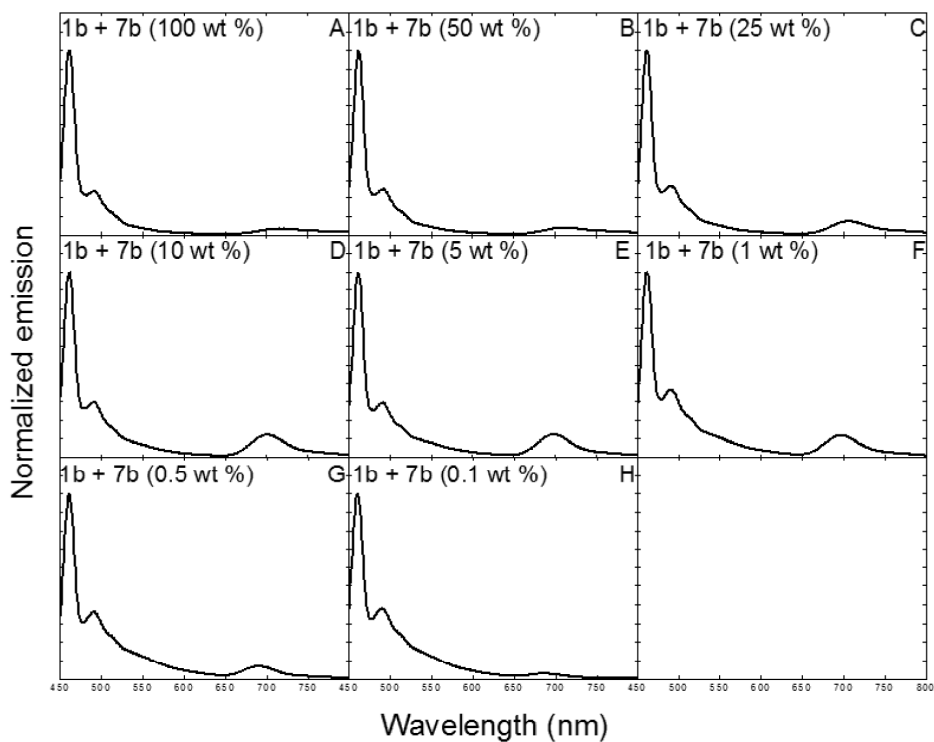**Figure S4:** Thin films of polymer **1b** and fluorophore **7a** at various fluorophore concentrations.

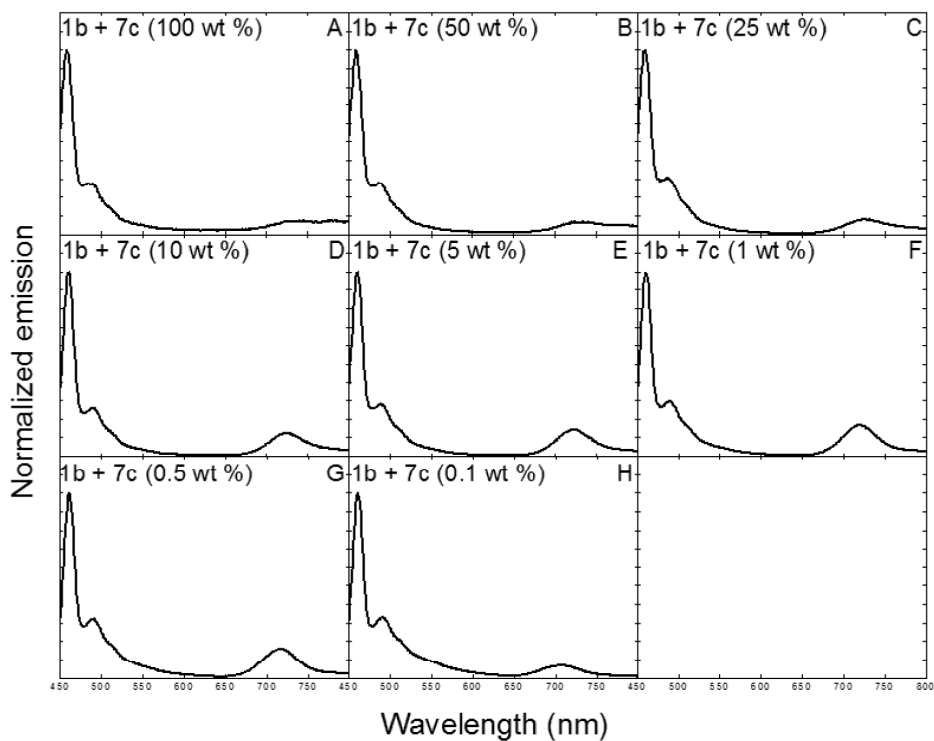**Figure S5:** Thin films of polymer **1b** and fluorophore **7b** at various fluorophore concentrations.

Figure S6: Thin films of polymer **1b** and fluorophore **7c** at various fluorophore concentrations.

*Y-axis expanded spectra of fluorophores **6c-7c** in thin films with polymer **1b** at various concentrations with direct fluorophore excitation:*
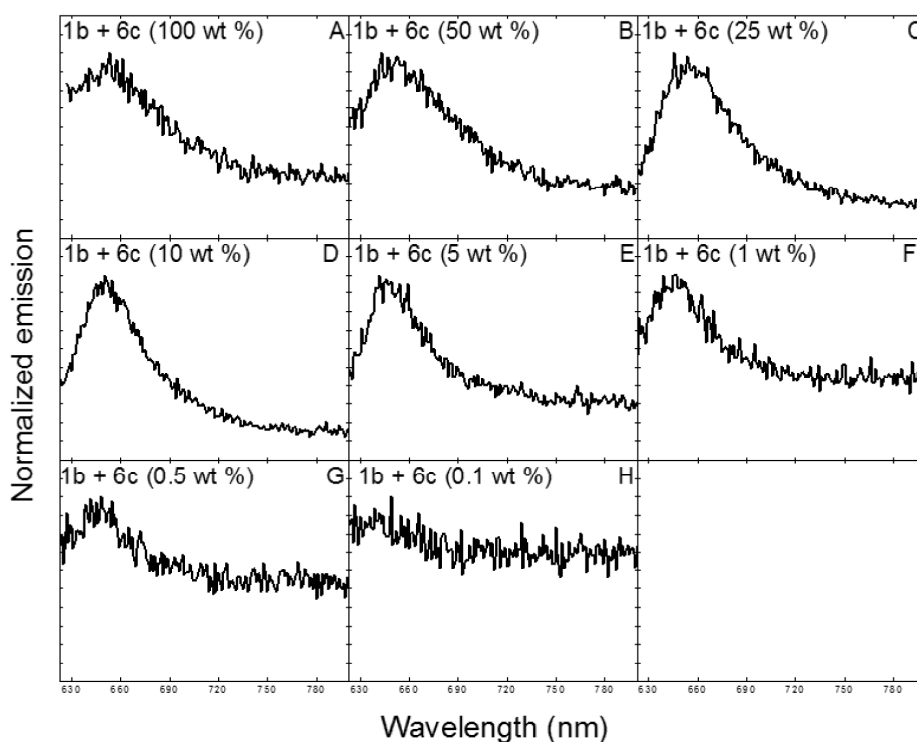

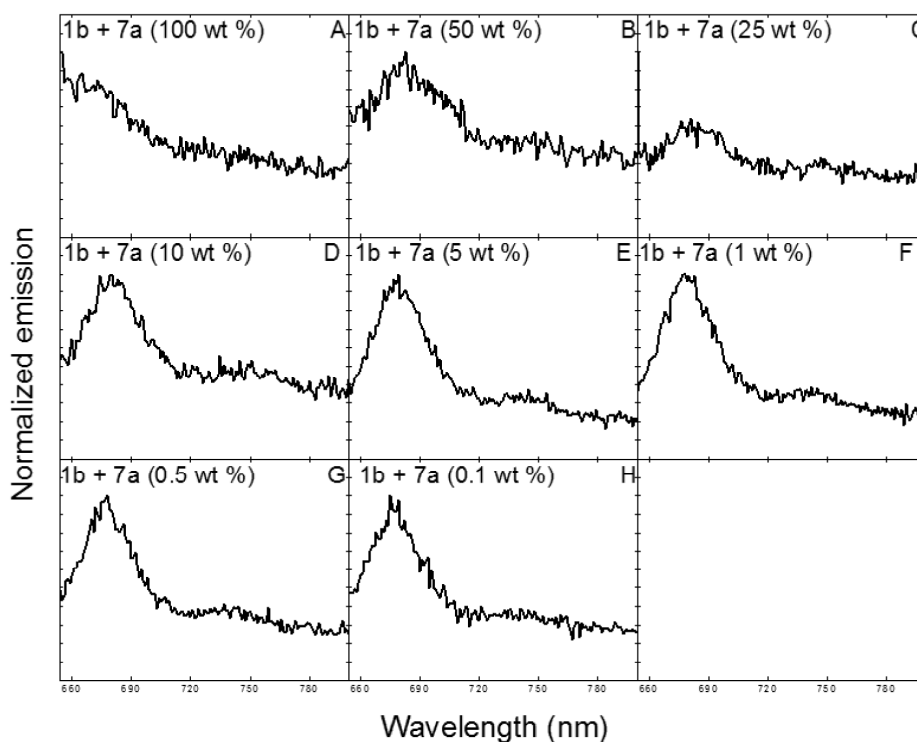**Figure S7:** Thin films of polymer **1b** and fluorophore **6c** at various fluorophore concentrations.

Figure **S8**: Thin films of polymer **1b** and fluorophore **7a** at various fluorophore concentrations.
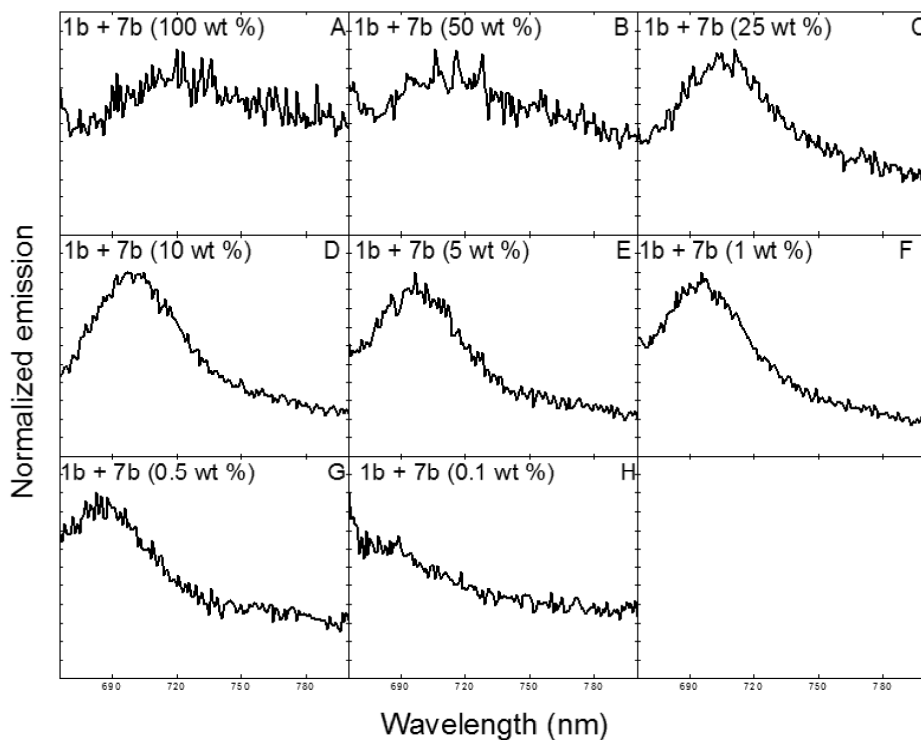
Figure **S9**: Thin films of polymer **1b** and fluorophore **7b** at various fluorophore concentrations.
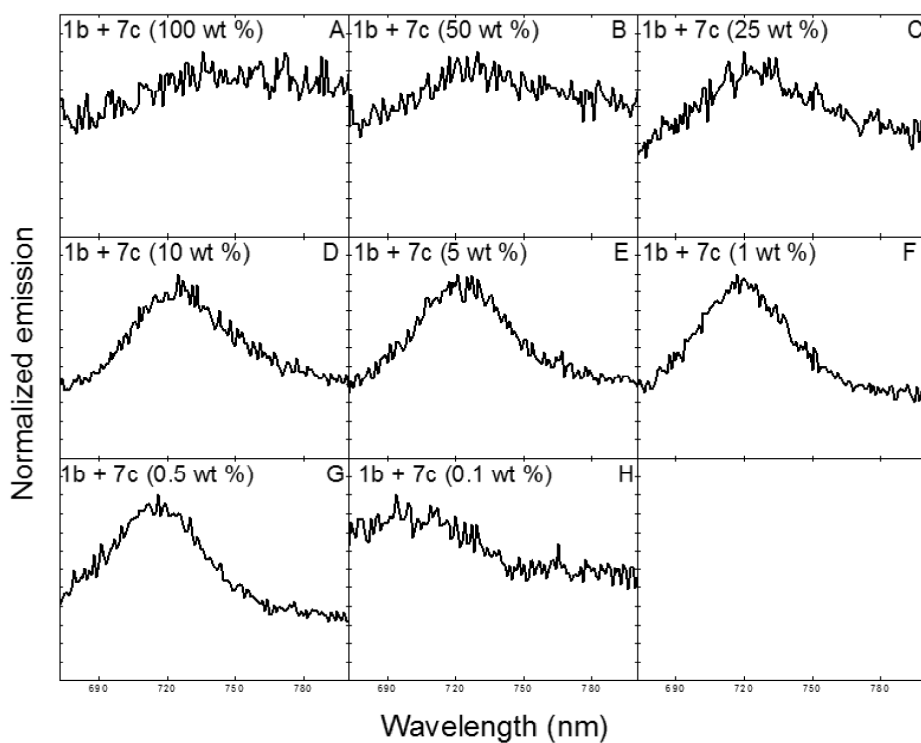

Figure **S10**: Thin films of polymer **1b** and fluorophore **7c** at various fluorophore concentrations.

Lifetime data tables

To obtain more information on the mechanism of energy transfer in the thin film blends, the excited state lifetimes of both the polymer and the fluorophore were measured and fit using either mono- or bi-exponential decay profiles (Table S7 and Table S8). With one exception (*vide infra*) the lifetimes of the polymer measured at low fluorophore concentration (0.1 weight %) and high fluorophore concentration (25 weight %) were constant. This invariance of lifetime with fluorophore concentration is indicative of a static quenching mechanism that occurs between two fluorophores in a self-quenching process.[3]

The exception to this trend was compound **7a**, and the lifetime of polymer **1b** at low fluorophore concentrations was substantially lower than its lifetime at high fluorophore concentration. This trend in fluorescence lifetime correlates with the efficiency of energy transfer in the films – *i.e.* more facile energy transfer at 0.1 weight % fluorophore (46.3-fold amplification compared to 7.3-fold at 25 weight %) provides an additional deactivation method for the polymer, leading to the shorter observed lifetime.

Table S7: Lifetimes of the excited state of polymer **1b** in thin film blends[a] and the values in parentheses are the percentages of each lifetime used to fit the experimental data.

Fluorophore	25 weight %	0.1 weight %
6c	0.80 ns (95.5 %)	0.70 ns (96.3 %)
	4.92 ns (4.5 %)	2.41 ns (3.7 %)
7a	1.22 ns (100 %)	0.79 ns (92.2 %)
		3.02 ns (7.8 %)
7b	0.71 ns (96.1 %)	0.93 ns (93.4 %)
	3.56 ns (3.9 %)	3.73 ns (6.6 %)
7c	0.78 ns (100 %)	0.77 ns (93.5 %)
		3.11 ns (6.5 %)

[a]These values are averages of lifetimes measured at three different spots in the same thin film.

Table S8: Lifetime of fluorophores in thin films with polymer **1b**[a]

Fluorophore	25 wt %	0.1 wt %
6c	1.39 ns (66.5 %)	1.54 ns (100 %)
	4.45 ns (33.5 %)	
7a	0.99 ns (93.4 %)	3.00 ns (100 %)
	3.00 ns (6.6 %)	
7b	1.19 ns (90.2 %)	2.95 ns (100 %)
	3.72 ns (9.8 %)	
7c	0.69 ns (84.3 %)	1.96 ns (82.9 %)
	2.65 ns (15.7 %)	3.84 ns (17.1 %)

[a] These values are averages of lifetimes measured at three different spots in the same thin film.

Supplementary tables:

Table S9: Absorption and emission of fluorophores in chloroform solution

Fluorophore	λ_{max} abs. (nm)	λ_{max} em. (nm)
6c	626	641
7a	555, 600, 655	674, 725
7b	619, 674	699
7c	626, 682	712

Table S10: Absorption and emission of fluorophores in thin films with polymer **1b**

Fluorophore	λ_{max} abs. (nm)	λ_{max} em. (nm)
6c	634	650
7a	615, 669	679
7b	629, 678	701
7c	631, 682	725

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[1] Olmsted, III. J. J Phys Chem 1979, 83, 2581.

[2] Osaheni, J. A.; Jenekhe, S. A. J Am Chem Soc 1995, 117, 7389.

[3] Lakowicz , J. R. Principles of Fluorescence Spectroscopy; Kluwer Academic/Plenum Publishers: New York, 1999; Chapter 13.