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Efficient and Tunable Fluorescence Energy Transfer via Long-Lived Polymer Excitons

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Abstract: A highly fluorescent polymer consisting of repeating pendant dye molecules, difluoroboron dibenzoylmethane (BF_2dbm), and an end-capped Rhodamine B (RhB) exhibits efficient energy transfer (EnT) owing to long-lived polymer excitons. External stimuli such as solvation and temperature can dramatically affect the efficiency of EnT and thus change the emission color.

Introduction

Excited-state energy transfer (EnT) involving high-density dye aggregates, where the efficiency of EnT is often dictated by the organizations of dye molecules,[1] is of fundamental and practical importance in optoelectronic research.[2] In nature, such a process is essential for the flow of energy and matter (e.g., photosynthesis).[3] In a single photosynthetic unit, hundreds of organized "antenna" dyes (e.g., chlorophylls and carotenoids) absorb solar light and transfer energy to reaction centers with high efficiency.[4] In this process, how the molecules are assembled or coupled is critical for rapid excitation EnT, which triumphs over other multiple competing processes (thermal quenching, fluorescence, etc.) during the lifetime of excited states.[5, 6] As such, better comprehension of EnT processes involving organized dye aggregates will not only help decode the mechanism of photosynthesis,[7, 8] but can also benefit the field of optoelectronics.[9, 10] For example, in order to elucidate the dynamics and kinetics in natural photosynthetic systems, studies of EnT in complicated systems have been approached by employing artificial counterparts,[11] where arrays of dye aggregates[12, 13] can be constructed through a series of techniques including supramolecular chemistry,[14-16] monolayers on surface,[17, 18] shell-core dendrimer,[19, 20] and functionalized polymers.[21, 22] Many of the systems were investigated in combination with fluorescence and laser spectroscopy due to its intrinsic advantages such as high temporal resolution and sensitivity. For instance, the kinetics of EnT polystyrene containing pendant luminescent donor/acceptor pairs of $Ru(bpy)_3^{2+}/Os(bpy)_3^{2+}$ and chemically modified $Ru(bpy)_3^{2+}$ derivatives[18, 23] has been thoroughly investigated with fast laser spectroscopy. The choice of heavy-metal containing luminophores is on the basis that longer-lived excited-state is important for high EnT yield. Nature however has chosen mainly organic dyes as light-harvesting molecules to generate long-lived excited states, and it is believed that the enigma lies in the manner the dyes are associated with each other.[3, 5, 6]

Here, we present the synthesis and spectroscopic properties of a *chemically well-defined* light-harvesting polymer via atom transfer radical polymerization (ATRP), consisting of repeating BF_2dbm donor pendants and an end-capped RhB acceptor (Scheme 1). This system allows for more definitive mechanistic investigations on EnT. To calculate the number-averaged molecular weight of the polymer, UV/Vis spectroscopy was used because the absorptions of Rhodamine acceptor (initiator) and BF_2dbm donar (monomer) can be well resolved. The polydispersity information, however, could be readily obtained from GPCs.

In previous reports, we found that BF_2dbm complexes could form various ground-state aggregates which generate long-lived solid-state[24] or polymer[25] excitons through polyermization-enhanced intersystem crossing (PEX). Firstly, we reason that the long-lived excitons generated by the the BF_2dbm polymer will boost the EnT process because optimal EnT conformations could be sampled with long-lived polymer donor lifetimes. Secondly, the EnT polymer should exhibit tunable emissions based on the types of intrachain and/or interchain aggregates formed. Such design enables synthesis via well-defined polymerization method such as ATRP by end-functionalization of an acceptor dye (RhB in this case). Finally, end-capped RhB with its emission spectrum well-separated from that of BF_2dbm can be conveniently used to monitor the EnT process.

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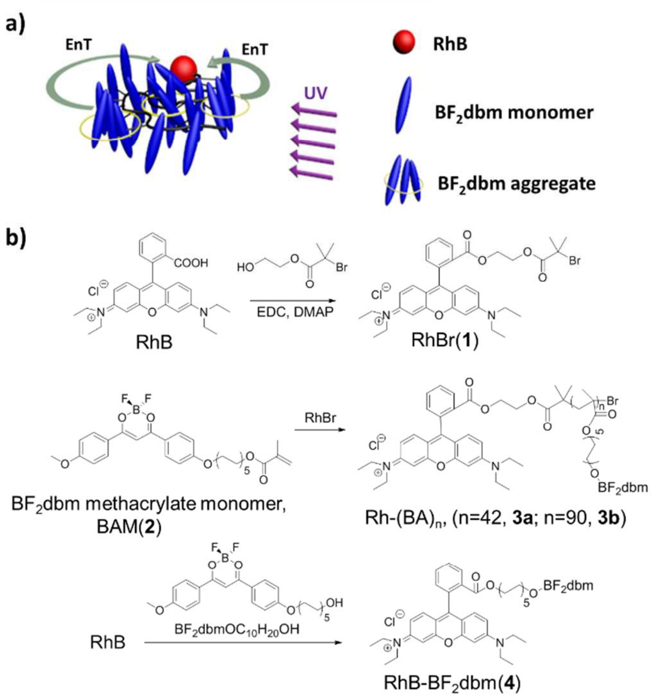

Scheme 1. a) Schematic illustration of Energy Transfer (EnT) within the Donor (BF$_2$dbm) - Acceptor (RhB) Polymer. b) Syntheses of Rhodamine B initiator (RhBr, **1**), boron methacrylate monomer (BAM, **2**), Rhodamine-end capped boron polymer [Rh-(BA)$_n$, **3a** and **3b**] and RhB-BF$_2$dbm (**4**).

We show that with an acceptor/donor ratio as low as ~1:90 in dilute solution, high EnT efficiency reflected in emission spectra can still be achieved in this linear polymer system. Such high EnT efficiency is very likely due to the formation of long-lived, optically forbidden excited states from intrachain aggregates, which function as *exciton reservoir* to continuously feed RhB fluorescence. Importantly, EnT can be controlled by solvent, temperature, and concentration, which are all related to donor aggregates formation. To gain further insights, a detailed theoretical study and ultra-fast laser spectroscopy were also performed, where we found that intrachain aggregates exhibit strongly split excited states facilitating efficient EnT. The study presents a new way of generating highly efficient organic polymer EnT systems without the need to introduce metal chromophores.

Results and Discussion

The BF$_2$dbm monomer was synthesized according our previous report. [25]The Rhodamine B (RhB) initiator, RhBr (**1**, Scheme 1), was obtained as a dark purple product by an esterification reaction between 2-hydroxyethyl-2-bromo-2-methylpropanoate and RhB after silica gel chromatography purification. RhBr-initiated atom transfer radical polymerizations (ATRP) of the boron methacrylate monomer (BAM, **2**) were conducted in N, N-dimethylformamide (DMF) at 70 °C for 12 h in oxygen-free conditions. After the reactions had ceased, ATRP of BAM (**2**) yielded red polymers [Rh-(BA)$_n$, **3a** (n ≈ 42, M$_n$ ≈ 22.5 kDa, PDI= 1.28) and **3b** (n ≈ 90, M$_n$ ≈ 49 kDa, PDI = 1.07, M$_n$ of polymer **3a** and **3b** is calculated from UV-Vis spectroscopy using absorption of compound **4** as the calibration standard, Figure 1] soluble in polar organic solvents such as dichloromethane (DCM), DMF and dimethyl sulfoxide (DMSO).

The optical properties of the EnT system were first studied in DMF, a good solvent for polymers. From UV-Vis spectra (Figure 1b), **3a** and **3b** have the same strong absorption peak at 418 nm and a very weak one at 561 nm, which are assigned to π-π* transitions of BF$_2$dbm donor and RhB acceptor moieties, respectively. However, the vibronic features of the polymer absorption spectra are different from those observed for monomer **2**: the high energy transition is strengthened, which can be ascribed to presence of intrachain H-aggregates[26] for polymers **3a** and **3b**. The steady-state fluorescence emission spectra of **3a** and **3b** were also investigated in dilute DMF solutions first (Figure 1c). Despite the low molar content of RhB initiator (~1-2%), the strongest emission peaks of polymers **3a** and **3b** in DMF are both around 587 nm, which is characteristic of RhB fluorescence. A shoulder peak at ~450 nm is also present, due to contribution from BF$_2$dbm fluorophores. From the emission spectra, **3a** is apparently more efficient in EnT than **3b**, as the blue emission shoulder is much smaller for **3a**. This is understandable because the average donor distance on **3a** is shorter, which is favorable for both direct fluorescence energy transfer and exciton migration.[27]

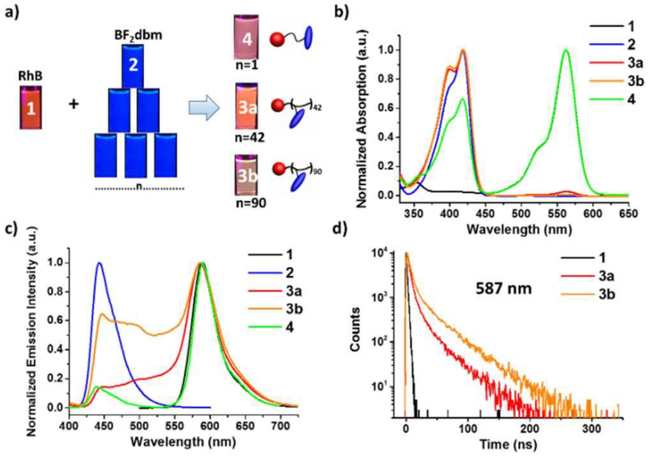

Figure 1. a) Pictorial demonstration of visual emission color changes before and after the polymerization in dilute DMF solutions under a handheld UV lamp (λ_{ex} = 365 nm); b) UV-Vis absorption spectra of RhB initiator **1** (black), BF$_2$dbm monomer **2** (blue), EnT polymers **3a** (red) and **3b** (orange) and **4** (green). Separate graphs see S1. c) steady-state emission spectra of RhB initiator **1** (1×10^{-5} mol/L, black), BF$_2$dbm monomer **2** (1×10^{-5} mol/L, blue), EnT polymers **3a** (5 μg/mL or 9×10^{-6} mol/L dye concentration, red), **3b** (5 μg/mL or 9×10^{-6} mol/L dye concentration, orange) and **4** (1×10^{-5} mol/L, green). c) Fluorescence decay profiles of **1** (black), **3a** (red), and **3b** (orange) at 587 nm. Separate graphs see S2.

Next, time-correlated fluorescence measurements were also performed to probe the EnT process within the complex polymer system in the excited state (Figure 1d and Table S2). The small molecules RhB and BF$_2$dbm derivatives **1** and **2** have single-exponential decays of 1.53 ns (587 nm) and 1.68 ns (447 nm) at the emission maxima in DMF, respectively. Polymers **3a** and **3b** on the other hand exhibit much more complicated decay profiles, depending on the emitting wavelengths selected. In the presence of a single RhB initiator, polymers **3a** and **3b** show quite different lifetimes: τ = 4.09 ns at 587 nm for 3a; τ = 7.26 ns at 587 nm for 3b. Compared to the lifetime of BF$_2$dbm aggregates (λ ~ 550 nm, τ = 29.7 ns, $\tau_{intrinsic}$=250 ns, reported by our previous work[25]), both **3a** and **3b** exhibit much shorter-lived excited states (9.40 ns for 3a and 15.96 ns for 3b). This is presumably quenched by RhB acceptor, which concomitantly exhibits increased lifetime as a result of excited-state EnT.

For polymers, solvents are known to influence chain conformations and thus play a pivotal role in intrachain EnT in solutions.[28] Figure 2a shows the emission of polymers **3b** in DCM, DMF and DMSO, where dramatically different spectroscopic features can be observed. In DMF, **3b** contain significant contribution from the blue emission (λ_F ~ 450 nm), suggestive of more donor monomer presence than in the other two solvents. In DCM and DMSO, the relative intensity of RhB fluorescence (λ_F ~ 587 nm) is significantly enhanced for **3b**, which implies more efficient EnT. This implies dye aggregates are more efficient EnT donors than monomers. It can be inferred that DMF has the best affinity towards BF_2dbm moieties so that the polymer chain is more extended, resulting in smaller equilibrium constant for intrachain aggregates formation as well as larger average donor-acceptor distance. The assumption may be further supported by comparing excitation spectra in DMF and DCM (Figure S3). In DMF, the excitation (λ_{max} = 417 nm monitored at 587 nm) is similar to that of absorption in Figure 2b, suggesting a combination of dye isolates and aggregates as donor species; in DCM, however, excitation spectrum monitored at 587 nm is characteristic of H-aggregates, with maximum peak blue-shifted for ~ 1460 cm^{-1} to 393 nm. The relatively large excitonic splitting is presumably due to large extinction coefficient as well as “face-to-face” arrangement of the dye molecules. Fluorescence lifetime measurements were also performed in DCM for polymers **3a** and **3b**. Compared to the data obtained in DMF, for both polymers, observed radiative decays at 587 nm are lengthened by almost a factor of three (**3a**: 4.09 to 11.1 ns; **3b**: 7.26 to 19.1 ns, Table S3), which is also likely due to more EnT contribution from longer-lived aggregates as donors, assuming they have comparable thermal decay rates in both solutions.

Temperature effect was explored in solution, where DMSO with high boiling point was used for maximal temperature range. Visually, the fluorescence emission of **3b** turned from orange to white when the solution was heated. The recorded fluorescence intensity ratio between 587 and 447 nm (rough indicator of EnT efficiency) shows a sharp decrease over a temperature range of 120 K (293 to 413 K, figure 2b, note that the spectra are presented in a 3D fashion to qualitatively show the trend. The standard 2D spectra are included in Figure S4). When the intensity ratio is plotted against temperature at an interval of 10 K, the data can be fit with an exponential relationship. Compared to the solvent effects, temperature-correlated study allows for somewhat more quantitative characterization of the EnT system. We here only attempt to explain observed data by taking into considerations of the two parameters used in solvent study: presence of intrachain aggregates and average donor-acceptor distance over temperature. From the solvent study, aggregates are likely more efficient in the EnT process, given its slow intrinsic fluorescence decay rate (ca. ~ 4×10^6 s^{-1} [25] vs. ca. ~ 5×10^8 s^{-1} for BF_2dbm monomer), as long-lived excited state can sample more favorable EnT orientations and thus increase EnT rate. This relates to the general relationship for EnT efficiency: $\eta = k_{EnT}/(k_{EnT} + k_F + k_{nr})$, where k_{EnT}, k_F, k_{nr} stand for rates of EnT, fluorescence, and non-radiative decay, respectively. This is also consistent with previous reports, where donors with much slower decay such as Tb (III)[29] and Ru (II)[30] complexes have been demonstrated to exhibit much higher EnT efficiency. In fact, even strictly optically forbidden H-aggregates can efficiently pass excited-state energy to acceptors.[31] Therefore, the EnT efficiency of RhB-$(BF_2dbm)_n$ polymers in solution should be related to the amount of long-lived excited-state aggregates present,[32] and should exponentially decrease with rising temperature due to loss of aggregates. Meanwhile, RhB-$(BF_2dbm)_n$ main chains are also likely to adapt more extended conformations at elevated temperatures, thus reducing the average donor-acceptor distance.

We finally investigated on how concentrations affect EnT for these polymers. One essential question regarding EnT in polymeric systems is that both intrachain and interchain pathways are possible. There have been many elegant and revealing studies on conjugated polymer systems by Schwartz,[33] Barbara,[34] and Brédas,[35] demonstrating that intrachain is the leading process for isolated polymer molecules while interchain EnT becomes dominating in the solid state. However, such studies are rare for *non-conjugated* dye-bearing polymer materials due to frequent aggregation-related quenching problems. In the present RhB-$(BF_2dbm)_n$ system, one marked advantage is that EnT can be conveniently manifested by well-resolved emission spectra from both donor and acceptor moieties at various experimental conditions. Figure 2c shows how steady-state emission spectra evolve over polymer concentration in DMF. For **3b**, acceptor (RhB) emission exhibits progressive enhancement at the cost of the donor (BF_2dbm) intensity when the concentration is increased over a factor of 100 (from 0.001 to 0.1 mg/mL), and achieves maximum relative intensity in the solid state. Since each RhB-$(BF_2dbm)_n$ molecule carries both acceptor and donor moieties, the data can be interpreted as increased interchain interactions among these polymers at in more concentrated solutions, which could be caused by diffusion-controlled bimolecular EnT.

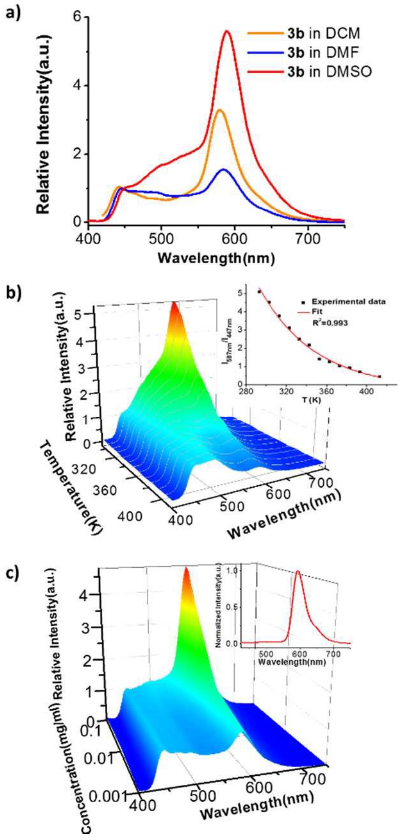

Figure 2. a) Steady-state emission spectra of polymers **3b** in DCM (orange), DMF (blue), and DMSO (red) (λ_{ex} = 385 nm). b) Steady-state emission spectra of polymers **3b** at different temperatures in DMSO (λ_{ex} = 385 nm); inset: data fitting of emission intensity ratio between 587 and 447 nm for **3b** (λ_{ex} = 385 nm). c) Steady-state emission spectra of **3b** as a function of polymer concentration in DMF and in the solid state (insets, solid emission spectra of **3b**, λ_{ex} = 385 nm).

Thus far, the “crude” fluorescence experiments have successfully demonstrated that linear $(BF_2dbm)_n$ polymers are well-suited as light-harvesting “antenna” for efficient EnT to RhB acceptor. To demonstrate the proposed aggregation-enhanced *exciton reservoir* mechanism, we have performed density function theory (DFT) calculations and also conducted ultrafast spectroscopy measurements to capture the transient population kinetics in polymer RhB-$(BF_2dbm)_{90}$ (**3b**) and RhB-BF_2dbm (**4**). Using a time-resolved pump–probe scheme spanning 1 ns with fs resolution, we have obtained absorbance change spectra in Figure 3a and 3b as a function of time delay between a 400 nm pump laser pulse and a 500-750 nm probe laser pulse. The differences between two samples are obvious, and can be best interpreted with the scheme based on our DFT calculations for BF_2dbm, RhB, and $(BF_2dbm)_7$ (analogous to the polymer) in Figure 3c. Firstly, electrons in both samples are excited to the LUMO or LUMO band at around - 3 eV by the 400 nm pump pulse. As non-radiative or thermal decay is weak due to big HOMO-LUMO gaps, and fluorescence occurs at ns scale, the probe laser is able to detect the positive signal of the excited state absorption (ESA) of BF_2dbm molecules in the ps domain. Based on the computed energy levels, ESA wavelength of BF_2dbm monomer is either < 560 nm or > 870nm, and cannot be detected by our probe pulse. On the other hand, the energy level splitting in polymers results in a large range of ESA signals from 600 to 1000 nm. It is worth to note that the ESA of RhB-$(BF_2dbm)_{90}$ goes up and down repeatedly in the ps region, which is a direct result of the two-way electron communication or BISC between the singlet and triplet manifolds. This in turn leads to long lifetime of excited electrons for enhanced EnT to the RhB moiety.

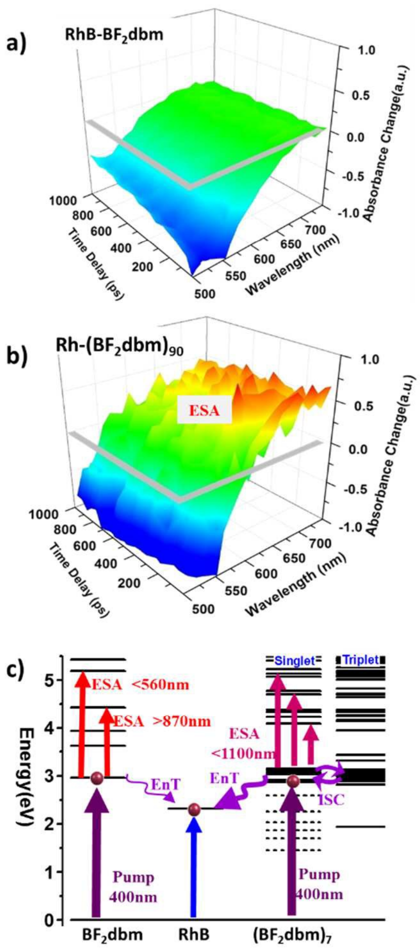

Figure 3. a) and b) Ultrafast absorbance change spectra (500-750) as a function of probe delay, recorded with a 400 nm pump. Red to blue color: positive to negative signals. c) The schematic illustration of how ultrafast spectroscopy characterizations reveal transient population kinetics, and the demonstration of BF_2dbm aggregation enhanced EnT process.

Conclusion

We have successfully synthesized well-defined fluorescent polymers consisting of repeating BF_2dbm donor units and an RhB chain-end polymers. These polymers exhibit high energy transfer (EnT) efficiency from linearly arranged blue-emitting donor “antenna” to a single orange-emitting RhB molecules upon photo-excitation. The EnT efficiency can be controlled by solvent, temperature, and concentration, which are related to the formation of BF_2dbm aggregates. Detailed theoretical calculations and ultra-fast laser spectroscopy studies on the donor-acceptor polymers reveal that in dilute solution intrachain BF_2dbm aggregates lead to more forbidden and nearly degenerate singlet and triplet states. Thus these aggregate species serve as an exaction reservoir after photo-excition, which is readily harvested by RhB acceptor dye and contributes to the observed high EnT efficiency. The model system shows that very efficient EnT can be realized through long-lived excited state in metal-free systems.

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1. V. Czikklely, H. Forsterling and H. Kuhn, *Chem. Phys. Lett.*, 1970, 6, 207-210.
2. M. A. Fox, *Acc. Chem. Res.*, 2012, 45, 1875-1886.
3. G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, *Nat. Chem.*, 2011, 3, 763-774.
4. V. Sundström, T. Pullerits and R. van Grondelle, *J. Phys. Chem. B*, 1999, 103, 2327-2346.
5. C. Y. Wong, R. M. Alvey, D. B. Turner, K. E. Wilk, D. A. Bryant, P. M. Curmi, R. J. Silbey and G. D. Scholes, *Nat. Chem.*, 2012, 4, 396-404.
6. G. S. Schlau-Cohen, A. Ishizaki, T. R. Calhoun, N. S. Ginsberg, M. Ballottari, R. Bassi and G. R. Fleming, *Nat. Chem.*, 2012, 4, 389-395.
7. S. Bode, C. C. Quentmeier, P.-N. Liao, N. Hafi, T. Barros, L. Wilk, F. Bittner and P. J. Walla, *Proc. Nati. Acad. Sci. USA*, 2009, 106, 12311-12316.
8. M. T. Colvin, A. B. Ricks, A. M. Scott, A. L. Smeigh, R. Carmieli, T. Miura and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2010, 133, 1240-1243.
9. N. S. Lewis and D. G. Nocera, *Proc. Nati. Acad. Sci. USA*, 2006, 103, 15729-15735.
10. R. Eisenberg and D. G. Nocera, *Inorg. Chem.*, 2005, 44, 6799-6801.
11. D. G. Nocera, *Acc. Chem. Res.*, 2012, 45, 767-776.
12. M. R. Wasielewski, *Acc. Chem. Res.*, 2009, 42, 1910-1921.

13. D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, 34, 40-48.
14. A. Jesorka, T. S. Balaban, A. R. Holzwarth and K. Schaffner, *Angew. Chem. Int. Ed. Engl.*, 1996, 35, 2861-2863.
15. A. Ajayaghosh, V. K. Praveen and C. Vijayakumar, *Chem. Soc. Rev*. 2008, 37, 109-122.
16. F. J. Hoeben, P. Jonkheijm, E. Meijer and A. P. Schenning, *Chem. Rev.*, 2005, 105, 1491-1546.
17. T. Gu, J. K. Whitesell and M. A. Fox, *Chem. Mater.*, 2003, 15, 1358-1366.
18. C. N. Fleming, K. A. Maxwell, J. M. DeSimone, T. J. Meyer and J. M. Papanikolas, *J. Am. Chem. Soc.*, 2001, 123, 10336-10347.
19. T. Gu, J. K. Whitesell and M. A. Fox, *J. Phys. Chem. B*, 2006, 110, 25149-25152.
20. L. Pu, *Macromol. Rapid Commun.s*, 2000, 21, 795-809.
21. Y. Sun, Z. Chen, E. Puodziukynaite, D. M. Jenkins, J. R. Reynolds and K. S. Schanze, *Macromolecules*, 2012, 45, 2632-2642.
22. M. Chen, K. P. Ghiggino, A. W. Mau, W. H. Sasse, S. H. Thang and G. J. Wilson, *Macromolecules*, 2005, 38, 3475-3481.
23. D. Ma, S. E. Bettis, K. Hanson, M. Minakova, L. Alibabaei, W. Fondrie, D. M. Ryan, G. A. Papoian, T. J. Meyer and M. L. Waters, *J. Am. Chem. Soc.*, 2013, 135, 5250-5253.
24. X. Sun, X. Zhang, X. Li, S. Liu and G. Zhang, *J. Mater. Chem.*, 2012, 22, 17332-17339.
25. X. Sun, X. Wang, X. Li, J. Ge, Q. Zhang, J. Jiang and G. Zhang, *Macromol. Rapid Commun.*, 2014, DOI: 10.1002/marc.201400529
26. H. Yamagata and F. Spano, *J. Chem. Phys.*, 2012, 136, 184901.
27. H. Lin, R. Camacho, Y. Tian, T. E. Kaiser, F. Wurthner and I. G. Scheblykin, *Nano Lett.*, 2009, 10, 620-626.
28. T.-Q. Nguyen, V. Doan and B. J. Schwartz, *J. Chem. Phys.*, 1999, 110, 4068-4078.
29. M. K. Johansson, R. M. Cook, J. Xu and K. N. Raymond, *J. Am. Chem. Soc.*, 2004, 126, 16451-16455.
30. C. N. Fleming, L. M. Dupray, J. M. Papanikolas and T. J. Meyer, *J. Phys. Chem. A*, 2002, 106, 2328-2334.
31. T. Kobayashi, T. Taneichi and S. Takasaka, *J. Chem. Phys.*, 2007, 126, 194705.
32. J.-H. Hsu, W. Fann, P.-H. Tsao, K.-R. Chuang and S.-A. Chen, *J. Phys.l Chem. A*, 1999, 103, 2375-2380.
33. T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz and S. H. Tolbert, *Science*, 2000, 288, 652-656.
34. J. Yu, D. Hu and P. F. Barbara, *Science*, 2000, 289, 1327-1330.
35. D. Beljonne, G. Pourtois, C. Silva, E. Hennebicq, L. Herz, R. Friend, G. Scholes, S. Setayesh, K. Müllen and J. Brédas, *Proc. Nati. Acad. Sci. USA*, 2002, 99, 10982-10987.