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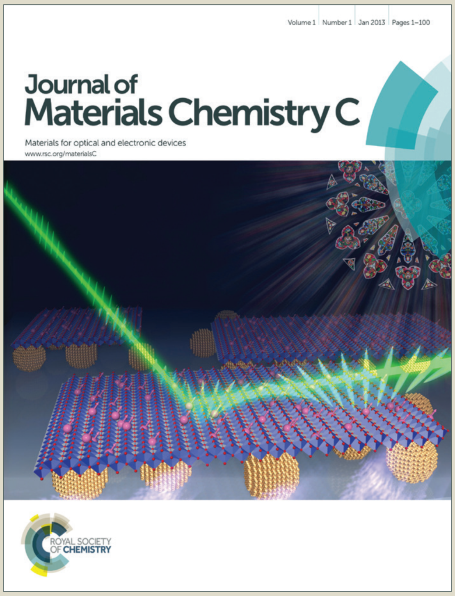

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Aggregation Enhanced Pure Violet Emission of a Spiral *Meta*-Polyfluorene by Supramolecular Control of Excimer Formation†

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In π-conjugated optoelectronic functional materials, the excimer in aggregate state drew much attention because of undesired low energy emission and fluorescence quenching. We report enhanced pure violet emission in *meta*-polyfluorene by restrained excimer formation in double-helix-like interchain entangled aggregates. It will be beneficial for optoelectric application of conjugated polymers, especially in the processing of film fabrication for high efficiency devices.

Introduction

In nature, supramolecular structures are vital important to the functions, e.g. the α-helices and β-sheet of protein supply totally different catalyzer site in biological reaction of living organisms.[1] Similarly, the artificial π-conjugated optoelectronic functional molecules have witnessed the supramolecular control in pivotal functionalstructures.[2] In the past decades, enormous efforts have been paid to mimic natural systems utilizing conjugated molecules especially with special optoelectronic function, e.g. light harvesting systems,[3] circular polarized luminescence,[4,5] photo switch,[6] enhanced photo current[7] and so on.[8]

The excimer[9] in organic photochemistry is a supramolecular structure with a dynamic dimeric molecule formed from two species, at least one of which is in its excited state. The excimer exhibits some consequential applications, such as in biophysics it is used to evaluate the distance between biomolecules and in organic chemistry many reactants react through an excimer or exciplex intermediates.[10,11] In π-conjugated molecules and polymers, the excimer is regarded as important light source.[12,13]

The excimer drew much attention because of its undesired red-shifted emission and low fluorescence efficiency. In blue/violet emissive fluorene based light emitting polymers, excimer and fluorenone emission are regarded as two of the most important origins of the low energy emission in visible color range (green/red).[14-20] Spirobifluorene have proved eliminates the possibility of fluorenone based on its different synthetic route with alkyl substituted-fluorene, which is good model compound for investigation of intermolecular interaction. The effect of linkage would directly related to the optical properties, because different effective conjugation lengths and intersegment packing mode. The *para*-linked polyspirobifluorene have been reported with well color purity, however in *meta*-linked polyspirobifluorenes and oligomers low energy emisssion has been observed.[21] In our previous work, we have testified the fluorene based excimer as origin of low energy emission in *meta*-linked polyspirobifluorene.[22] Different with structural defects, the excimer formation is the nature of π-conjugated system, which is availably formed by the tight packing of π-molecules (or π-segments) with the distance of smaller than 4.0 Å.[23] In previous works, the reported effective strategy to suppress excimer emission focus on increasing the intermolecular distance, such as the introducing of big substitution and cycloalkane coating,[24-27] but it may cause some negative effects for the comprehensive performance of materials for optoelectronic applications, such as lowing charge mobility, and morphology stability as the results of weakened intermolecular interactions. In this work, the excimer emission is successfully retrained in the solid of conjugated polymer PsF36 (Figure 1A) as they assembled into tight chain entanglements, which shows enhanced violet emission.

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†Electronic Supplementary Information (ESI) available: Experimental section, synthesis and characterization of PsF36, ^{1}H NMR spectrum of PsF36, fluorescence spectra of PsF27 in mixture solvent, fluorescence spectra of PsF36 in mixture solvent and the absorbance at 270nm and unaggregated fraction. See DOI: 10.1039/c000000x/

Experimental section

All chemical and reagents were purchased from Sigma-Aldrich. All solvents were carefully dried and purified before use.

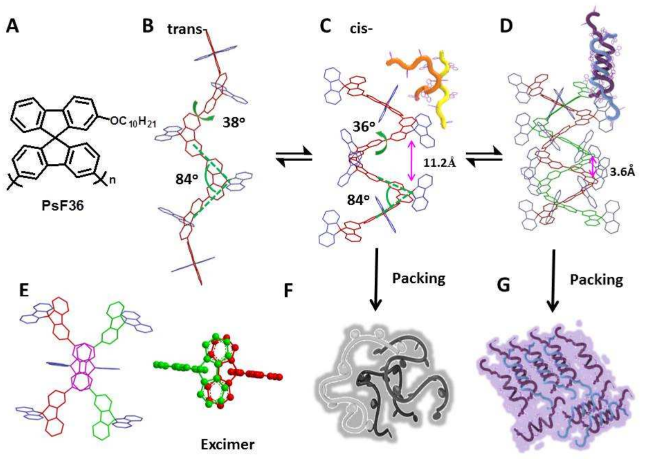

Figure 1. (A) Chemical structure of PsF36, (B) conformation of all *trans*-isomer, (C) conformation of all *cis*-isomer, (D) formation of double chain in PsF36 with *cis*-conformation, (E) the excimer formation in single chain packing, (F) the single chain packing with low fluorescence, and (G) the double chain packing with high pure violet emission.

In experiment, the dilute PsF36 tetrahydrofuran (THF) solution was put in 55 ℃ water bath, and then the poor solvent water was added to THF solution drop by drop within one hour, and finally temperature of water bath was decreased naturally to room temperature to induce assembly of PsF36 chains. As-prepared spiral *meta*-polyspirobifluorene were divided into two parts: the first portion was direct for UV-vis-NIR and PL spectra measurements. The second portion was spin-coated onto HOPG substrate for AFM characterization.

^{1}H NMR (300MHz) spectra were obtained using a Bruker 300M spectrometer with tetramethylsilane as an internal standard. GPC analysis was conducted with a Waters GPC 2410 in THF using a calibration curve of polystyrene standards. UV-vis-NIR absorption spectra were recorded using a Shimadzu UV-3600 spectrophotometer. PL spectra were obtained with a Horiba JY FluoroMax-4P Luminescence spectrometer. AFM experiments were carried out under ambient condition by using a Veeco Multi Mode Nanoscope IIIa system operating in tapping mode. All the measurements were done at room temperature. The ground-state geometries of *cis-*/*trans*-conformation in spirobifluorene dimers were optimized at the B3LYP level of theory using the basis set of 6-31G (d, p) without symmetry restrictions. Aggregate of two spirobifluorenes in excimer/ground-state aggregate, the chain structure with different conformation and double chain entanglement were optimized by MM+ of molecular mechanics. The DFT and MM+ calculations are carried out in the Gaussian 09 and Materials Studio program package, respectively.

Results and discussion

The chemical structure of PsF36 is shown in Figure 1A.[22] The number-average molecular weights (Mn) of PsF36 is 14,000 (PDI = 1.9), where each polymer chain possesses ~30-60 repeat units on average. In the case of *meta*-linked PF36, 3-position of a fluorene unit is linked with 6-position of an adjacent fluorene unit. As view the stereographic projection of five member-ring in the fluorene units, there are two different conformations: *cis*-conformation (five member-ring on the same side), *trans*-conformation (five member-ring on the opposite sides) (Figure 1B, C). The rotation of single carbon bond between adjacent phenyl is a typical biphenyl structure, which has two symmetrical stable distortional conformations at ±30-40^o, respectively. For the axes angle between two *meta*-linkage is ~84^o (Figure 1B, C), these two conformations of biphenyl caused a completely different chain conformation in the polymer chain structure of PsF36. The chain conformations would be described as two extreme structures in the long range: 1) when axes angle twists to the same direction, the *cis*-PsF36 polymer chain with intendancy to form spiral structure; 2) when axes angle twists to the opposite direction, *trans*-PsF36 polymer chain would form a wormlike structure (Figure 1B, C), where the actual polymer chains are mixture of the two conformations. The distortional angle in the optimized molecular conformation is 36 and 38 degrees in *cis*- and *trans*-conformation respectively, and the total energy of molecules with different conformations are basically consistent ($\Delta E = 0.35$ kcal mol^{-1}) according to DFT calculation. The ratio of *cis*- and *trans*-conformation is 36%, and 64% at room temperature according to maxwell-boltzmann distribution. Experimentally estimated by ^{1}H NMR spectrum, the ratio of *cis*- and *trans*-conformation is 33% and 67% by integral area accounts in $CDCl_3$ at room temperature (Figure S1),[28] which indicates a high content of *cis*- conformation in balanced states.

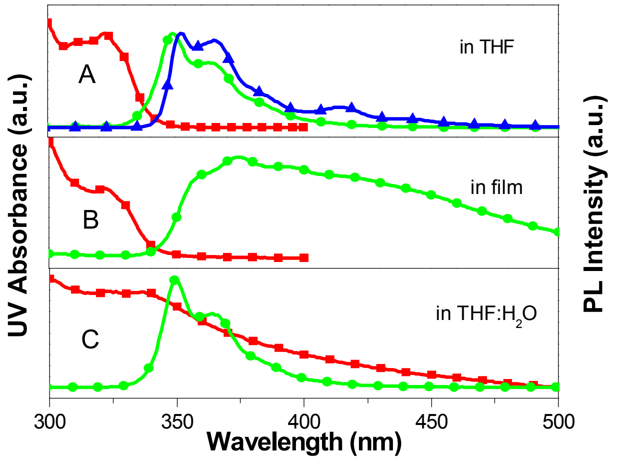

Figure 2. The absorption (square) and fluorescence (round and triangle) spectra of (A) PsF36 in THF, 1.5×10^{-5} M (round), 2.1×10^{-3} M (triangle); (B) PsF36 spin-coated film from THF solution; (C) PsF36 in THF:H_2O mixed solution 1.5×10^{-5} M (THF:H_2O = 7:3).

PsF36 exhibits low energy emission at high concentration of its good solvents such as $CHCl_3$, toluene and THF, which is from excimer emission.[22] Figure 2A, B show the absorption and PL spectra of PsF36 in THF solution and spin-coated film (single polymer chain and random aggregation), respectively. PsF36 has the absorption maximum at 320 nm and emission band at 350 nm due to a π-π* transition derived from conjugated backbone. The fluorescence is quenched dramatically when the concentration is increased and two new emission bands at 420, 440 nm have been observed. In spin-coated film from THF solution, low energy emission appears as a broad band, which turns the violet/ultraviolet emission to blue, although the absorption is similar with that in diluted solution. As shown in Figure 1E, the excimer conformation between intersegments is the reversed face-to-face of two adjacent fluorene units, including the interaction between two fluorene units on main chain and local big chain distortion based on *cis*-conformation.[22]

As dropwise adding H_2O in PsF36 THF solution, the presence of the poor solvent would induce the shrink of polymer chain. Based on the principle of polymer chain scale we propose poor solvent make chain conformation from *trans*- to *cis*- and the aggregation of polymer chains results in the formation of small aggregates.(Figure 1B, C) The aggregate suspends in the solution of THF/H_2O mixture exhibiting spectral behaviors of totally different with that in its good solvent. As shown in Figure 2C, the emission spectra of PsF36 in THF/H_2O mixture solvent are the similar shape and peak positions with that in dilute good-solvent solution. No additional low energy emission has been observed. The corresponding absorption spectrum is also different with that in its good solvent. The absorption spectrum of PsF36 in THF/H_2O mixture solvent has a new extinction band with a 20 nm redshift compared with bulk absorption, which would come from the absorption of new aggregate and/or the light scattering of aggregate. It indicates the control of excimer formation in poor solvent induced aggregate which is different with that from good solvent (Figure 2B spin-coated film from THF solution). The β-phase of *para*-linked polyfluorenes has been reported redshifted absorption behavior, which from the decreased distortional angle and increased conjugation.[29,30] But, for *meta*-linkage of fluorene units (effectively broken the conjugation), the poor solvent induced conformation change plays little role on the effective conjugation length, thus spectral change in PsF36 would be not from the conformation change as in the β-phase of *para*-linked polyfluorenes. As additional evidence, there is no redshift in emission of PsF36, which indicates the new absorption is not from the distortion of adjacent units (the emission of PsF27[20] in the same condition shows a typical redshifted β-phase emission as in Figure S2).

It is logical but interesting to observe that the fluorescence is obviously enhanced in the suspension in THF/H_2O compared with the reference in pure THF solvent, where the supramolecular excimer formation is effectively controlled. The evolution of PL intensity in mixture solvent is displayed in Figure S3 (1.5×10^{-5} M) and Figure 3 (7.5×10^{-5} M). In the low concentration in Figure S3 (1.5×10^{-5} M) about 80% enhancement has been observed with H_2O ratio of 50%. In higher concentration in Figure 3 (7.5×10^{-5} M) the aggregate can be induced more effectively, nearly 2.5-fold enhancement has been observed with H_2O ratio of 25%. As the black square in inset of Figure 3, the PL intensity normalized by that in pure THF is shown as a function of H_2O ratio. The emission enhancement is weak when the H_2O ratio lower than 20%, and become very effective after this critical H_2O ratio. The apparent photoluminescence quantum yields (PLQY) in the mixed THF/water systems with the different ratio are displayed in inset of Figure 3. For the emission quenching is different in different concentration, the absolute PLQY is as a function of concentration. Thus in this work the PLQY in the mixed THF/water systems with the different ratio is expressed as apparent PLQY normalized by the PLQY in THF solution with the same concentration. As shown in inset of Figure 3, the PLQY enhancement is more obvious than PL, with nearly 7-fold enhancement has been observed with H_2O ratio of 25%. It indicates that the poor solvent induced intersegment aggregate play important role on emission enhancement. To our knowledge there is little report on aggregate enhanced emission (AEE)[31,32] in polyfluorene derivatives and this phenomenon is only observed in *meta*-linked PF but not *para*-linked ones (PsF27 as in Figure S2).

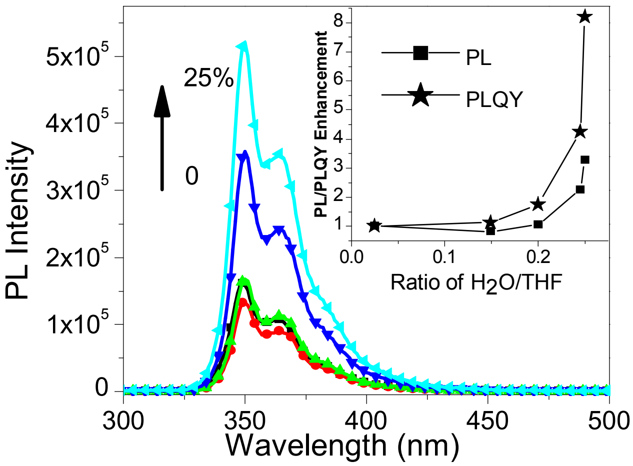

Figure 3. Fluorescence spectra ofPsF36 in THF:H_2O (7.5×10^{-5}M) as a function of H_2O ratio. The spectra were measured at the excitation wavelength of 280nm. The inset shows the evolution of relative PL intensity at 350 nm and apparent PLQY as a function of H_2O ratio, which is normalized by PL intensity and PLQY of PsF36 in THF (7.5×10^{-5}M).

By theoretical simulation, the fluorene-fluorene distance is 11.2 Å in single chain with all *cis*-conformation, where the interchain crossover is still allowed for excimer formation (Figure 1E, F) and makes low fluorescence. In order to understand the obstacle of excimer formation by direct random chain packing, we propose the presence of poor solvent not only induce the shrink of polymer chain from *trans*- to *cis*-conformation but also give additional double chain entanglement in order to avoid the interaction with poor solvent. Figure 1D shows the tight entangled double chains of two

PsF36 chains with all *cis*-conformation from theoretical simulation, where the reversed face-to-face packing would be forbidden both within double chain and in the advanced packing of tight entangled double chain helix (Figure 1G). Thus the possibility of excimer formation would be very low in presence of poor solvent and not visible experimentally, and the effective violet emission is emerge which is the character of *meta*-linked polyfluorene. Especially the nearest fluorene-fluorene distance is 3.6 Å in double chain model, which is the distance for π-π-interaction and similar as that in excimer conformation (Figure 1D).[22] It indicates that by this way the obstacle of excimer is not related with the increase of intermolecular distance and would not disturb electric properties like mobility for optoelectronics application. In addition, taking the two adjacent spirobifluorene units with distance of 3.6 Å in double chain model as the original conformation, the theoretical simulation indicates that the intermolecular dimer structure has an energy minimum in the conformation of double chain entanglement. However its energy is 3.9 kcal mol^{-1} higher than the conformation of "reversed face-to-face" for excimer formation. It means that this conformation is unstable when exists separately in nature. Here we suppose the double chain entanglement would stabilize this aggregate structure, thus the double chain structure with tight chain entanglements plays the key role in the excimer control and enhanced emission.

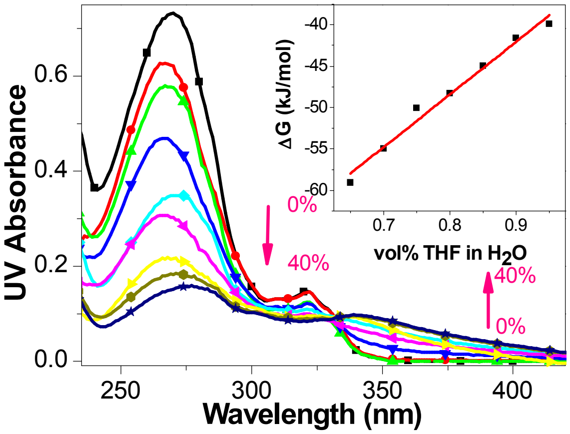

Figure 4. Detailed absorption spectra of PsF36 (1.5×10^{-5} M) as a function of THF:H$_2$O ratio. The inset shows Gibbs free energy change (Δ*G*) as a function of THF ratio.

The detailed absorption spectra of PsF36 as a function of THF:H$_2$O ratio is conducted as in Figure 4 in order to explore the thermodynamic driving forces for PsF36 aggregate. The intensity of new band at ~330 nm increases with the ratio of poor solvent with a clear isobestic point, which indicates the transformation between two species. With the increased fraction of water from 0% to 40%, a substantial decreasing of absorption at 270 nm and increasing of absorption at 340nm express the aggregation. For a two state equilibrium process between single chain (S) and double chain (D) aggregate (Equation (1)), we can analyze the solvent dependent UV-vis spectra from Figure 4 to determine the equilibrium constants K_{eq} and the free energy changes Δ*G* for aggregate in the respective solvent.[33]

$$2S \xleftrightarrow{K_{eq}} D \quad (1)$$

By assuming that the respective absorbance values at 270 nm A_{THF} in pure THF and A_{H2O} in the highest ratio of H$_2$O, the mole fraction of unaggregated single chain α_{unagg} can be expressed as Equation (2):

$$\alpha_{unagg} = \frac{A - A_{H2O}}{A_{THF} - A_{H2O}} \quad (2)$$

As shown in Figure S4, the absorbance at 270 nm and the related unaggregated fraction displayed as a function of THF volume ratio. For each solvent composition, the K_{eq} and Δ*G* (Figure 3 inset) can be calculated according to Equation (3) and Equation (4):

$$K_{eq} = \frac{[D]}{[S]^2} = \frac{c_T(1-\alpha_{unagg})}{c_T^2\alpha_{unagg}^2} \quad (3)$$

$$\Delta G = -RT \ln K_{eq} \quad (4)$$

c_T is the total concentration of PsF36. An approximatively linear dependency between the free energy change and solvent ratio is obtained. The free energy change decreases with the ratio of THF, which indicates the role of poor solvent water in aggregate.

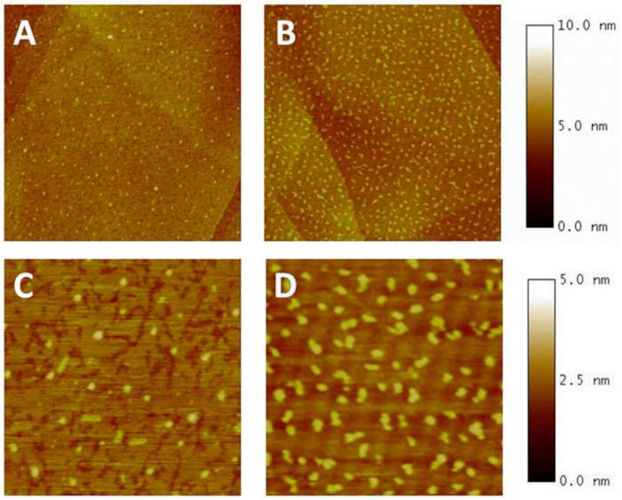

Figure 5. AFM height images of PsF36 spin-coated on HOPG plate substrates (A, C) from THF solution at a concentration of 1×10^{-5} M (by repeat unit); (B, D) from THF:H$_2$O mixed solution, THF:H$_2$O = 3:1 at concentration of 1.5×10^{-5} M. (A, B) 3×3 μm^2; (C, D) 1×1 μm^2.

Figure 5B, D show AFM height images of PsF36 spin-coated onto HOPG plate substrates from THF/H$_2$O solution (THF:H$_2$O

= 3:1, concentration of PsF36 is 1.5×10^{-5} M), while the images from THF solution are given in Figure 5A, C as a comparison. Without poor solvent water, PsF36s behave as small amount of additional particles and lamellars (21 nm), which would correspond to single polymer chain. After addition of poor solvent water, it is replaced by more particles with bigger size (37 nm). It indicates the presence of poor solvent effectively induce the entanglement of polymer chain, which is consistent with the results of thermodynamics. The aggregate size is much bigger than the size of single/double polymer chain, thus the morphology in 1.5×10^{-5} M with THF:H_2O = 3:1 is proposed as the double chain packing as shown in Figure 1G. The reversed face-to-face packing for excimer formation (Figure 1D) would be forbidden during the molecular packing of tight entangled double chains, where high pure violet emission emerges.

Conclusion

In summary, we have reported poor solvent induced the chain assemblies of PsF36, where the well color purity with enhanced emission is achieved. It is originated that the low energy emission of PsF36 from the excimer in amorphous films is effectively restrained in presence of poor solvent with the tight chain entanglements and the structural ordered packing. It is a good example that supramolecular assembly can induce new optoelectronic function. This result will inspire new ideas for conjugated polymers, especially in the processing of film fabrication for high efficiency devices. In future work, we will try to prepare aggregate by other poor solvent with low boiling point like methanol, which may benefit for device application.

Acknowledgements

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References

1 J. D. Watson and F. H. C. Crick, *Nature* 1953, **171**, 737-738.

2 F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. Schenning, *J. Chem. Rev.* 2005, **105**, 1491-1546.

3 a) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell and N. W. Isaacs, *Nature* 1995, **374**, 517-521; b) T. Pullerits and V. Sundström, *Acc. Chem. Res.* 1996, **29**, 381-389; c) X. Hu, T. Ritz, A. Damjanović, F. Autenrieth and K. Schulten, *Q. Rev. Biophys.* 2002, **35**, 1-62.

4 T. Shiraki, Y. Tsuchiya, T. Noguchi,; S. Tamaru, N. Suzuki, M. Taguchi, M. Fujiki and S. Shinkai, *Chem. Asian J.* 2014, **9**, 218-222.

5 K. Watanabe, K. Suda and K. Akagi, *J. Mater. Chem. C* 2013, **1**, 2797-2805.

6 A. Khan, C. Kaiser and S. Hecht, *Angew. Chem. Int. Ed.* 2006, **45**, 1878-1881.

7 A. Zitzler-Kunkel, M. R. Lenze, K. Meerholz and F. Würthner, *Chem. Sci.* 2013, **4**, 2071-2075.

8 M. Wolffs, N. Delsuc, D. Veldman, N. VânAnh, R. M. Williams, S. C. J. Meskers, R. A. J. Janssen, I. Huc and A. P. H. J. Schenning, *J. Am. Chem. Soc.* 2009, **131**, 4819-4829.

9 Th. Förster, *Angew. Chem., Int. Ed.* 1969, **8**, 333-343.

10 P. Hammarström, B. Kalman, B. H.Jonsson and U. Carlsson, *FEBS Lett.* 1997, **420**, 63-68.

11 H. Yoshidaa, J. Arakia, J. Sonodaa, H. Nohtaa, J. Ishidaa, S. Hiroseb and M. Yamaguchi, *Anal. Chim. Acta* 2005, **534**, 177-183.

12 D. Thirion, M. Romain, J. Rault-Berthelot and C. Poriel, *J. Mater. Chem.*, 2012, **22**, 7149-7157.

13 C. Poriel, J. Rault-Berthelot, D. Thirion, F. Barrière and L. Vignau, *Chem. Eur. J.* 2011, **50**, 14031-14046

14 Y. Q. Mo, X. Jiang and D. R. Cao, *Org. Lett.* 2007, **9**, 4371-4373.

15 M. Gaal, E. J. W. List and U. Scherf, *Macromolecules* 2003, **36**, 4236-4237.

16 J. I. Lee, G. Klaerner and R. D. Miller, *Chem. Mater.* 1999, **11**, 1083-1088.

17 U. Lemmer, S. Heun, R. F. Mahrt, U. Scherf, M. Hopmeier, U. Siegner, E. O. Göbel, K. Müllen and H. Bässler, *Chem. Phys. Lett.* 1995, **240**, 373-378.

18 U. Scherf and E. J. W. List, *Adv. Mater.* 2002, **14**, 477-487.

19 K. L. Chan, M. Sims, S. I. Pascu, M. Ariu, A. B. Holmes and D. D. C. Bradley, *Adv. Funct. Mater.* 2009, **19**, 2147-2154

20 C. Poriel, N. Cocherel, J. Rault-Berthelot, L. Vignau and O. Jeannin, *Chem. Eur. J.* 2011, **17**, 12631-12645

21 Y. G. Wu, J. Li, Y. Q. Fu and Z. S. Bo, *Org. Lett.* 2004, **6**, 3485-3487.

22 Y. Q. Mo, L. Y. Du, L. L.Liu, J. C.Huang, Y. Y.Pan, B. Yang, Z. Q.Xie and Y. G. Ma, *J. Phys. Chem. C* 2013, **117**, 27081-27087.

23 F. L. Minn, J. P. Pinion and N. Filipescu, *J. Phys. Chem.* 1971, 75, 1794-1798.

24 F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorì, J. P. Rabe, M. J. O'connell, P. N. Taylor and H. L. Anderson, *Nat. Mater.* 2002, **1**, 160-164

25 C. J. Pan, K. Sugiyasu, Y. Wakayama, A. Sato and M. Takeuchi, *Angew. Chem. Int. Ed.* 2013, **52**, 10775-10779

26 W. L. Yu, J. Pei, W. Huang and A. J. Heeger, *Adv. Mater.* 2000, **12**, 828-831

27 J. Y. Lin, W. S. Zhu, F. Liu, L. H. Xie, L. Zhang, R. D. Xia, G. C. Xing and W. Huang, *Macromolecules*, 2014, **47**, 1001-1007

28 N. Fomina and T. E. Hogen-Esch, *Macromolecules* 2008, **41**, 3765-3768.

29 D. D. C. Bradley, M. Grell, X. Long, H. Mellor, A. Grice, M. Inbasekaran and E. P. Woo, *Proc. SPIE* 1997, **3145**, 254-259.

30 L. Huang, X. N. Huang, G. N. Sun, C. Gu, D. Lu and Y. G. Ma, *J. Phys. Chem. C* 2012, **116**, 7993-7999.

31 Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.* 2011, **40**, 5361-5388.

32 Y. N. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.* 2009, 4332-4353.

33 V. Dehm, M. Büchner, J. Seibt, V. Engel and F. Würthner, *Chem. Sci.* 2011, **2**, 2094-2100.

Graphical Abstract for:

Aggregation Enhanced Pure Violet Emission of a Spiral *Meta*-Polyfluorene by Supramolecular Control of Excimer Formation

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Violet emission of meta-polyfluorene is enhanced by restrained excimer formation in double helix-like inter chain entangled aggregates.

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