PCCP

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name

ARTICLE

Supramolecular Aggregates with Distinct Optical Properties from PDI Oligomers of Similar Structures

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

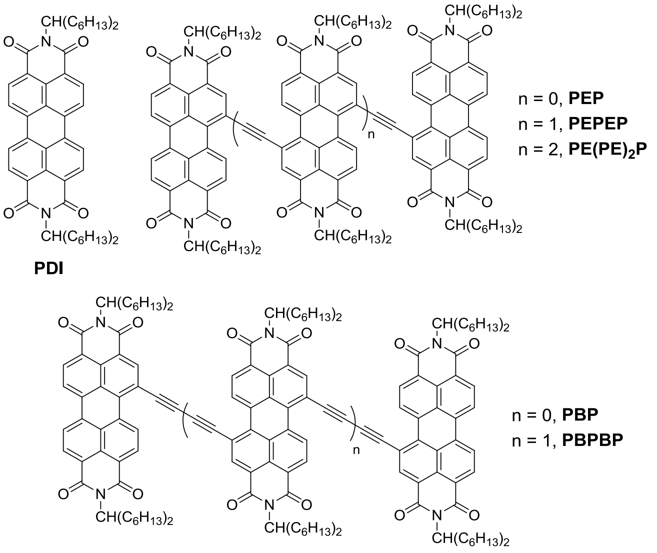
Qifan Yan, Kang Cai and Dahui Zhao*

The self-assembly behaviors of two series of monodispersed oligomers consisting of perylenediimide (PDI) linked by ethynylene and butadiynylene spacers are investigated in solutions. In spite of the very similar chemical structures, the two sets of oligomers manifest completely different optical properties upon self-aggregation, implying differed aggregate structures. While the oligomers containing butadiynylene spacers form H-aggregates, those featuring ethynylene linkers display J-aggregation characteristics. Thermodynamic analysis revealed the self-association constants of both series of oligomers increase with the number of PDI units in the backbones. Oligomers containing the same number of PDI units but different spacers display nearly identical enthalpy changes. According to the molecular exciton theory, the observed H- and J-aggregates are suggested to comprising similar packing motifs with slightly varied slipping angles, giving rise to greatly disparate optical properties.

Introduction

The self-organization of chlorin derivatives into so-called J-aggregates (or Scheibe aggregates)[4] has long attracted great attention, because they are important models for devising artificial photosynthetic systems.[1-4] By virtue of an array of appealing optical properties, such as red-shifted absorption with enhanced oscillator strength, J-aggregates promise great potentials in a range of applications, including organic photoconductor,[5] resonator,[6] light-emitting diodes,[7] photovoltaics,[8] nonlinear optics,[9] light-harvesting,[10] sensory materials,[11] and so on.[12] According to the molecular exciton theory,[13] all the unique properties of J-aggregates arise from a delocalized excitonic band formed by coherently coupled transition dipoles of monomers arranged in an ordered, slipped stacking motif. The ability to control the molecular assembly architectures and thereby realize J-aggregates through rational molecular design is highly desirable.[14,15] However, devising J-aggregates with polycyclic aromatic systems are challenging,[16] because H-aggregates often present a significant competition for exhibiting greater aromatic stacking surface area and larger enthalpy gain. Perylenediimide (PDI) is a representative example of such polycyclic aromatic systems. Most of its derivatives[17] display a strong propensity for H-aggregation.[18] Previous reported J-aggregates of PDI derivatives typically entailed careful deployment of H-bonds and/or steric hindrance, to override or modulate the face-to-face stacking tendency of PDI units.[19]

Chart 1. Chemical structures of studied PDI oligomers



Here, we present the unique self-assembly behaviors of two series of PDI oligomers of very similar chemical structures (Chart 1).[20] By switching the linker group joining the PDI subunits from butadiynylene to ethynylene, a transition from H- to J-aggregate is realized, as evidenced by the distinctive optical properties. A systematic investigation on the aggregation properties in solution show that the self-aggregation strength of the oligomers increases with the number of incorporated PDI units. In spite of the different linker and aggregate structures, oligomers comprising the same

---

Beijing National Laboratory for Molecular Sciences, Department of Applied Chemistry, Centre for Soft Matter Science and Engineering, Key Lab of Polymer Chemistry & Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China. Email: dhzhao@pku.edu.cn.

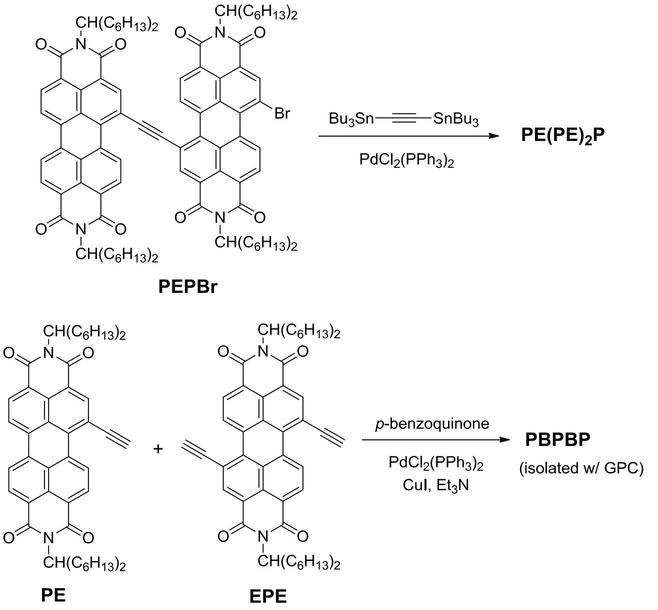
Electronic Supplementary Information (ESI) available: synthetic procedures and characterization data. See DOI: 10.1039/x0xx00000x

number of PDI units display nearly identical enthalpy changes in self-association, suggesting that the corresponding H- and J-aggregates likely possess very similar intermolecular stacking areas. Namely, the greatly differed optical properties may simply result from small variations in the slipping angles of monomer packing motifs. This phenomenon is explainable with the molecular exciton theory, which predicts that H- and J-aggregates could arise from similar face-to-face stacking motifs, and a small difference in the monomer stacking angle can bring about significant optical behaviour changes.[13]

Results and discussion

Materials.

Two series of PDI oligomers of varied chain lengths, featuring either ethynylene or butadiynylene linkers, are synthesized (Scheme 1). Molecules **PEP**, **PEPEP** and **PBP** were prepared as previously reported.[20,21] The synthesis of tetramer PE(PE)$_2$P was accomplished by coupling 1,2-bis(tributylstannyl)acetylene with two equivalents of mono-brominated PDI dimer (**PEPBr**) via Stille reactions (Scheme 2). Under modified Glaser conditions, hetero-coupling between mono- and diethynyl-substituted PDIs (**PE** and **EPE**) afforded PBPBP, which was isolated from a mixture of oligomers with varied size using the preparative gel-permeation chromatography (GPC). The structures of all newly synthesized oligomers were characterized by NMR and mass spectroscopy (ESI).



Scheme 1. Syntheses of trimeric and tetrameric PDI oligomers.

Self-aggregations of PEP and PBP.

Dichloromethane is a good solvent for these PDI oligomers (see SI for synthetic details),[20,21] and no ordered molecular aggregate is observed in this solvent (Figures S2 and S3). In contrast to the CH$_2$Cl$_2$ solutions, significant absorption band shape changes are displayed by the oligomers at varied concentrations and temperatures in aliphatic solvents, suggesting the occurrence of intermolecular aggregation. First of all, the rather different spectral behaviors of the two dimers, **PEP** and **PBP**, are studied.

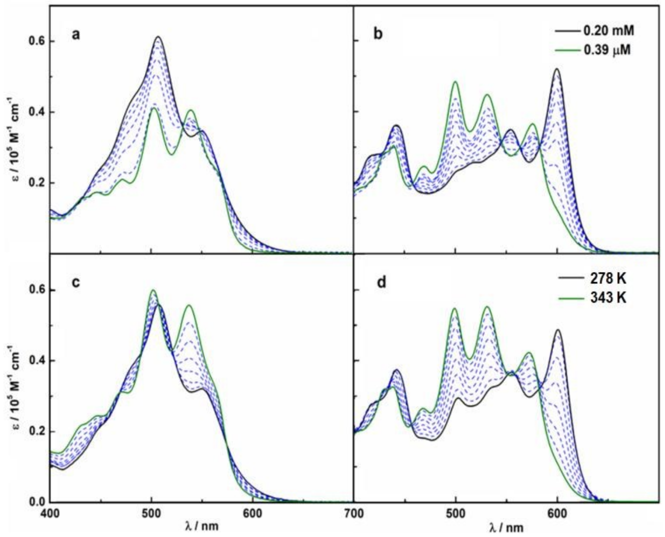


Figure 1. Concentration- (a-b, at 288 K) and temperature- (c-d, at 10 μM) dependent absorption spectra of **PBP** (a, c) and **PEP** (b, d) in cyclohexane.

At lower concentrations (<1 μM), the absorption band of **PBP** in CH is nearly identical to that in CH$_2$Cl$_2$ solution. As the solution concentration increases, a peak of shorter wavelength at about 510 nm escalates and eventually becomes the dominant peak (Figure 1a), suggesting that **PBP** undergoes a self-aggregation in CH at higher concentrations. A very similar spectral change is observed when the solution is cooled from 343 to 278 K (Figure 1c). Since no evident self-association is observed with **PDI** in the same concentration and temperature range (Figure S5), the enlarged aromatic skeleton of **PBP** apparently confers enhanced intermolecular association strength. The significantly quenched emission of **PBP** in the aggregated state also confirms the H-type aggregates (Figure S6).[18]

Interestingly, **PEP** displays vastly different concentration- and temperature-dependent spectra from those of **PBP**. At the sub-micromolar concentration level, nearly identical absorption bands are collected from **PEP** in CH and CH$_2$Cl$_2$. As the concentration increases from 0.4 μM to 0.2 mM in CH, the original peaks at 576, 531 and 500 nm gradually disappear, while two new peaks emerge at 600 and 554 nm, with multiple isosbestic points manifested (Figure 1b). As the solution temperature is lowered from 343 to 287 K, very similar spectral changes are exhibited (Figure 1d), indicating that **PEP** undergoes a J-type aggregation in CH, with a bathochromic shift of about 690 cm^{-1} (from 576 to 600 nm) in the 0-0 transition. The emission quantum efficiency of **PEP**[20b] increases slightly in CH from 0.1 μM to 10 μM (Figure S6), with perceptible narrowing in the band width. A small Stokes shift of 18 nm is displayed by the aggregate. All these properties are in agreement with the J-aggregate formation.

H- and J-aggregates of higher oligomers.

The absorption band of **PBPBP** in CH greatly resembles that of **PBP**, suggesting that **PBPBP** may also have assumed H-aggregates in CH. No significant absorption band shape change indicative of aggregate dissociation is shown by **PBPBP** in CH or dodecane upon diluting to sub-micromolar concentration or heating 373 K (Figure 2a), suggesting the much stronger association strength of this trimer than **PBP**. Toluene is then employed as an alternative solvent. Although the absorption spectrum of **PBPBP** at 273 K in toluene is similar to that from dodecane solution, a spectrum much resembles that shown in CH_2Cl_2 solution appears at 373 K, with the major peak red shifted from 517 to 544 (Figure 2b), indicative of H-aggregate dissociation of **PBPBP** at higher temperatures in toluene. Similar **PBPBP** H-aggregate dissociation is also observed at lower concentration in toluene (Figure S7).

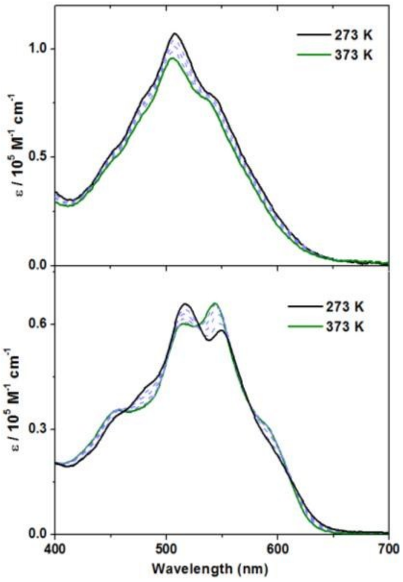


Figure 2. Temperature-dependent absorption spectra of **PBPBP** in dodecane (a, 2 μM) and toluene (b, 10 μM).

A much red-shifted absorption maximum (λ_{max}) at 675 nm is displayed by **PEPEP** in CH relative to that in CH_2Cl_2. When the CH solution is warmed from 278 to 343 K, this long-wavelength peak progressively attenuates, while the absorptions around 600 and 550 nm gradually increase (Figure 3a). The peak at 675 nm is thus assigned to be the J-band of **PEPEP**. The J-aggregate stability of **PEPEP** is substantially tempered in toluene, since the J-band around 680 nm is only partially developed at lowered temperature (*e.g.*, near 273 K) with relatively high concentration of **PEPEP** (Figure 3b).

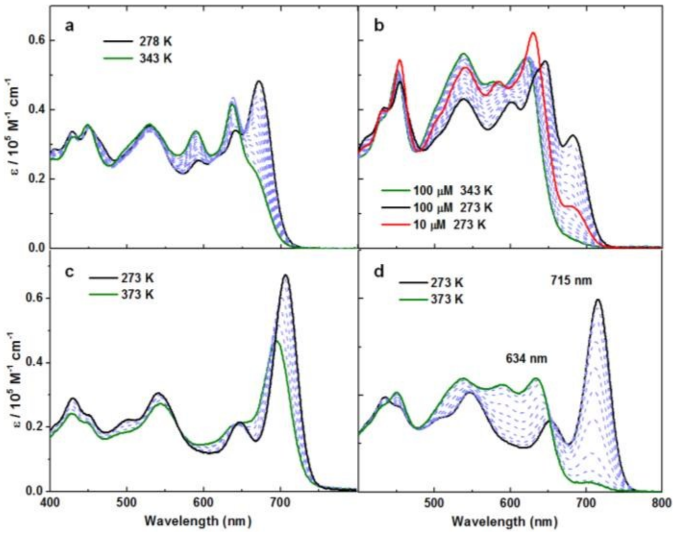


Figure 3. Temperature-dependent absorption spectra of **PEPEP** (a-b) and **PE(PE)$_2$P** (c-d) in cyclohexane (a, at 0.84 μM), dodecane (c, 5 μM), and toluene (b and d at 10 μM).

The absorption spectra of **PE(PE)$_2$P** in CH, dodecane and toluene are nearly identical at room temperature, with λ_{max} around 710 nm much red shifted compared to that in CH_2Cl_2. With a large extinction coefficient and relatively narrow FWHM (full width at half maximum), this major peak is assigned to be the J-band of **PE(PE)$_2$P**. This J-band persists upon heating to 373 K in dodecane (Figure 3c) with slight attenuation in the intensity, suggesting partial but incomplete dissociation of the J-aggregate. Even when the toluene solution is diluted to ca. 10^{-6} M, minimal J-aggregate dissociation occurs (Figure S8), confirming that very stable J-aggregate is formed by **PE(PE)$_2$P**. The J-aggregates of **PE(PE)$_2$P** are only mitigated at elevated temperature in toluene, indicated by the substantially reduced extinction coefficient at 710 nm and progressively increased absorption around 630 nm. At 373 K, **PE(PE)$_2$P** displays a spectrum in toluene very similar to that in CH_2Cl_2 (Figure 3d).

Aggregate structure analysis.

Assuming the self-association behaviors of these PDI oligomers following the isodesmic model, the extinction coefficient data are fitted to the van't Hoff equation as a function of temperature, to assess the thermodynamic parameters of the aggregates (Table 1).[22] The negative values of enthalpy and entropy changes indicate that the aggregations in these solvents are enthalpy-driven and entropy-disfavored processes for all studied oligomers. Very similar enthalpy changes (ΔH) are calculated for **PEP** and **PBP** in CH, as well as for **PEPEP** and **PBPBP** in toluene. Such comparable ΔH values strongly suggest that in the aggregated states the aromatic stacking areas are comparable for oligomers incorporating the same number of PDI units, and the thus molecular packing motifs are likely similar for the two series of oligomers. Moreover, the ΔH ratio of **PEPEP** to **PE(PE)$_2$P** in toluene is ca. 3 to 4. The estimated ΔH value of **PEP** in toluene (Table 1), obtained by applying a literature reported Gibbs binding energy ratio of pertinent solvents,[23] is also consistent with the trend that the molecular packing surface areas are roughly in proportion to the oligomer chain lengths, implying that the same intermolecular stacking motifs are assumed by the same series of oligomer.

Table 1. Aggregation type and thermodynamic parameters of aggregates

	Aggregate type	ΔH (kJ·mol^{-1})	ΔS (J·K^{-1}·mol^{-1})	K^a (M^{-1})
PBP[b]	H	-48 (-32)	-52	5.2×10^5
PEP[b]	J	-47 (-31)	-63	1.0×10^5
PBPBP[c]	H	-48	-66	9.6×10^4
PEPEP[c]	J	-48	-90	4.7×10^3
PE(PE)$_2$P[c]	J	-63	-105	3.6×10^5

[a] Self-association constants at 298 K calculated from ΔH and ΔS. [b] data from cyclohexane solution; data in parentheses are estimated ΔH values in toluene, obtained by applying the Gibbs binding energy ratio (~1.5) of toluene and (methyl)cyclohexane given for PDI dyes in ref 23. [c] data from toluene solution.

Based on the molecular exciton theory,[13] the absorption energy difference between the free molecule and aggregate can be estimated using the following equation:

$$\Delta E = \mu^2/(4\pi\varepsilon_0 d^3/\cos^3\theta) \times (1 - 3\cos^2\theta) \qquad (1)$$

where ΔE is the energy difference between the absorption maxima of the aggregate and free molecule, μ is the transition dipole moment of the free molecule, ε_0 is the permittivity in vacuum, d is vertical stacking distance between the molecules in the aggregated state, and θ is the slipping angle assumed by the transition dipoles with respect to the line drawn between the molecule centroids (Figure 4a). For polycyclic aromatic molecules, the π-π stacking distance (d) is a relatively invariable value. When ΔE is plotted as a function of θ, the sign of ΔE depicts a transition from negative to positive, corresponding to a switch from J- to H-aggregate, as θ crosses over the critical value of 54.7° (Figure 4a).[13]

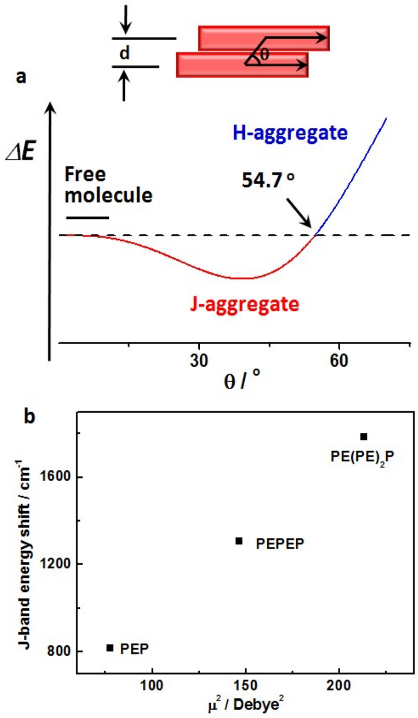


Figure 4. (a) Plot of ΔE *vs.* θ based on Eq. (1) with a constant d (exciton coupling of two choromphores is considered; arrows in the molecular stacking representation represent the transition dipole moments); (b) J-band energy shifts of **PEP**, **PEPEP** and **PE(PE)$_2$P** *vs.* respective square of transition dipole moment.

TD-DFT calculations reveal that the $S_0 \rightarrow S_1$ transition dipole moments of **PEP**, **PEPEP**, and **PE(PE)$_2$P** are similarly oriented nearly along the long axis of the molecules, with magnitudes of 8.8, 12.1 and 14.6 Debye respectively (Figure S17). Using the absorption maximum data, ΔE values of these three oligomers are determined, which impressively show an almost linear dependence on the square of transition dipole moments (Figure 4b). With similar d values, such a linear correlation reflects that **PEP**, **PEPEP**, and **PE(PE)$_2$P** exhibit nearly identical θ values. Such a conclusion is in agreement with the thermodynamic analysis results, suggesting that very similar molecular packing motifs are adopted by the three J-aggregated oligomers. Using a representative π–π stacking distance (d) of 0.35 nm applied to Eq. (1), approximate values of ca. 53° are estimated for the three J-aggregates, very close to the critical value of 54.7°.

It is perceivable from Figure 4a that around this critical value, significant E differences may arise from small variations. Although Eq. (1) is derived from a simplified model,[24,25] the exciton coupling theory makes a rational prediction that H- and J-aggregates may arise from similar molecular aggregates that only differ slightly in θ. Such a situation may just have occurred to our PDI oligomers. Considering the comparable ΔH values (Table 1), it is reasonable to assume that **PBP** and **PBPBP** might exhibit θ values similar to those of **PEP** and **PEPEP** but just fall in the range of H-aggregate. In spite of the minor differences in θ, the opposite signs of ΔE values bring about the dissimilar spectral properties.

A tentative rationale is proposed to explain why the ethynylene-linked oligomers adopt slightly smaller θ values than the butadiynylene analogues. The space-filling models reveal that in oligomers joined by butadiynylene spacers certain distance are left between the PDI units, whereas ribbon-shaped (though not completely planar) structures are formed by the oligomer comprising shorter ethynylene linkers (Figure S18). Taking **PBP** and **PEP** as examples, in the face-to-face aggregated state,[26] if a similar (smaller) θ angle was adopted by both molecules, a greater portion of the polycyclic framework of **PBP** would be exposed to the gap region between the PDI units (Figure S19), resulting in a smaller stacking area than that of **PEP**. Likely for such a reason, a slightly larger θ angle is assumed by **PBP**, for compensating the stacking area.

Conclusions

In summary, two series of PDI oligomers with similar chemical structures exhibit drastically differed optical properties. Oligomers comprising butadiynylene spacers assume the H-aggregates, whereas ethynylene-linked oligomers undergo J-aggregation. With progressively elongated oligomer chains, stronger self-association tendencies are detected, and for the J-aggregates increasingly red-shifted J-bands are observed, reasonably due to the enlarged transition dipole moments. Thermodynamic analyses suggested that the drastically disparate optical properties of the H- and J-aggregates may arise from small structural differences in the molecular packing motifs. Moreover, band-shaped molecules appear to be favourable for J-aggregate formation, because such molecules are more tolerant of the slipped packing motif. Relatively smaller stacking surface area is necessarily sacrificed by molecules of such shapes in adopting the largely slipped, face-to-face stacking motif.

Acknowledgements

This work is supported by the National Natural Science Foundation (No. 21174004, 21222403, and 51473003).

Notes and references

1 (a) T. Pullerits and V. Sundström, *Acc. Chem. Res.*, 1996, **29**, 381-389; (b) J. M. Olson, *Photochemistry and Photobiology*, 1998, **67**, 61-75; (c) R. E. Blankenship, *Molecular Mechanisms of Photosynthesis* Blackwell: Oxford, 2002.

2 T. Balaban, H. Tamiaki, A. Holzwarth, *Chlorins Programmed for Self-Assembly Supermolecular Dye Chemistry* F. Würthner, Ed. Springer Berlin/Heidelberg: 2005; Vol. 258, pp 585-585.

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) M. R. Wasielewski, *Acc. Chem. Res.* 2009, **42**, 1910-1921; (c) S. Sengupta, D. Ebeling, S. Patwardhan, X. Zhang, H. Berlepsch, C. Böttcher, V. Stepanenko, S. Uemura, C. Hentschel, H. Fuchs, F. C. Grozema, L. D. A. Siebbeles, A. R. Holzwarth, L. Chi and F. Würthner, *Angew. Chem. Int. Ed.*, 2012, **51**, 6378–6382; (d) S. Sengupta and F. Würthner, A*cc. Chem. Res.*, 2013, **46**, 2498-2512.

4 (a) D. Möbius, *Adv. Mater.*, 1995, **7**, 437-444; (b) F. Würthner, T. E. Kaiser and C. R. Saha-Moller, *Angew. Chem. Int. Ed.*, 2011, **50**, 3376-3410.

5 (a) P. M. Borsenberger, A. Chowdry, D. C. Hoesterey and W. Mey, *J. Appl. Phys*., 1978, **49**, 5555-5564; (b) B. J. Walker, A. Dorn, V. Bulovi and M. G. Bawendi, *Nano Lett.*, 2011, **11**, 2655–2659.

6 (a) J. R. Tischler, M. S. Bradley and V. Bulovi, *Opt. Lett.*, 2006, **31**, 2045-2047; (b) J. R. Tischler, M. Scott Bradley, Q. Zhang, T. Atay, A. Nurmikko a nd V. Bulović, *Org. Elec*., 2007, **8**, 94-113.

7 J. R. Tischler, M. S. Bradley, V. Bulović, J. H. Song and A. Nurmikko, *Phys. Rev. Lett.*, 2005, **95**, 036401.

8 P.-A. Bouit, D. Rauh, S. Neugebauer, J. L. Delgado, E. D. Piazza, S. p. Rigaut, O. Maury, C. Andraud, V. Dyakonov and N. Martin, *Org. Lett.*, 2009, **11**, 4806-4809.

9 (a) Y. Wang, *J. Opt. Soc. Am. B*, 1991, **8**, 981-985; (b) S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1992, 217; (c) N. T. Fofang, N. K. Grady, Z. Fan, A. O. Govorov and N. J. Halas, *Nano Lett*., 2011, **11**, 1556–1560.

10 R. Takahashi and Y. Kobuke, *J. Am. Chem. Soc.*, 2003, **125**, 2372-2373.

11 (a) K. E. Achyuthan, T. S. Bergstedt, L. Chen, R. M. Jones, S. Kumaraswamy, S. A. Kushon, K. D. Ley, L. Lu, D. McBranch, H. Mukundan, F. Rininsland, X. Shi, W. Xia and D. G. Whitten, *J. Mater. Chem.*, 2005, **15**, 27-28; (b) D. G. Whitten, K. E. Achyuthan, G. P. Lopez and O.-K. Kim, *Pure Appl. Chem.*, 2006, **78**, 2313-2323; (c) W. Liang, S. He and J. Fang, *Langmuir*, 2014, **30**, 805-811.

12 (a) J. M. W. Chan, J. R. Tischler, S. E. Kooi, V. Bulovic and T. M. Swager, *J. Am. Chem. Soc.*, 2009, **131**, 5659-5666; (b) S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu and M. Takeuchi, *Nat. Chem*., 2014, **6**, 188-195; (c) S. Ogi, T. Fukui, M. L, Jue, M. Takeuchi and K. Sugiyasu, *Angew. Chem. Int. Ed.*, 2014, **53**, 14363-14367**;** (d) M. Gsänger, E. Kirchner, M. Stolte, C. Burschka, V. Stepanenko, J. Pflaum and F. Würthner, *J. Am. Chem. Soc.*, 2014, **136**, 1564-1579.

13 M. Kasha, H. R. Rawls and M. A. El-Bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371-392.

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

15 J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte and A. E. Rowan, *Adv. Mater.*, 2006, **18**, 1251-1266.

16 K. Cai, J. Xie and D. Zhao, *J. Am. Chem. Soc*., 2014, **136**, 28-31.

17 (a) F. Würthner, *Chem. Commun.*, 2004, 1564-1579; (b) H. Langhals, *Helv. Chim. Acta*, 2005, **88**, 1309-1343; (d) M. R. Wasielewski, *J. Org. Chem.*, 2006, **71**, 5051-5066; (c) C. Huang, S. Barlow and S. R. Marder, *J. Org. Chem.*, 2011, **76**, 2386-2407; (e) C. Zhan and A. D. Q. Li, *Curr. Org. Chem.*, 2011, **15**, 1314-1339. (f) F. Würthner, C. R. Saha-M ӧller, B. Fimmel, S. Ogi, P. Leowanawat and D. Schmidt, *Chem. Rev.*, DOI: 10.1021/acs.chemrev.5b00188.

18 (a) J. Wang, A. Kulago, W. R. Browne and B. L. Feringa, *J. Am. Chem. Soc.*, 2010, **132**, 4191-4196; (b) H. Szelke, S. Schübel, J. Harenberg and R. Krämer, *Chem. Commun.*, 2010, **46**, 1667-1669.

19 For examples, see: (a) T. E. Kaiser, H. Wang, V. Stepanenko and F. Würthner, *Angew. Chem. Int. Ed.*, 2007, **46**, 5541-5544; (b) S. Ghosh, X.-Q. Li, V. Stepanenko and F. Würthner, *Chem. Eur. J.*, *2008*, **14**, 11343-11357; (c) T. E. Kaiser, V. Stepanenko and F. Würthner, *J. Am. Chem. Soc.*, 2009, **131**, 6719-6732; (d) H. Wu, L. Xue, Y. Shi, Y. Chen and X. Li, *Langmuir*, 2011, **27**, 3074-3082. (e) Z. Xie, V. Stepanenko, K. Radacki and F. Würthner, *Chem. Eur. J.*, 2012, **18**, 7060 -7070.

20 (a) Q. Yan and D. Zhao, *Org. Lett.*, 2009, **11**, 3426-3429; (b) J-W. Cho, H. Yoo, J.-E. Lee, Q. Yan, D. Zhao and D. Kim, *J. Phys. Chem. Lett.*, 2014, **5**, 3895-3901.

21 F. Würthner, V. Stepanenko, Z. Chen, C. R. Saha-Möller, N. Kocher and D. Stalke, *J. Org. Chem.*, 2004, **69**, 7933-7939.

22 R. B. Martin, *Chem. Rev.*, 1996, **96**, 3043-3064.

23 (a) Z. Chen, B. Fimmel and F. Würthner, *Org. Biomol. Chem.*, 2012, **10**, 5845-5855; (b) J. Schmidt, R. Schmidt and F. Würthner, *J. Org. Chem.*, 2008*,* **73***,* 6355-6362.

24 R. F. Fink, J. Seibt, V. Engel, M. Renz, M. Kaupp, S. Lochbrunner, H.-M. Zhao, J. Pfister, F. Würthner and B. Engels, *J. Am. Chem. Soc.*, 2008, **130**, 12858-12859.

25 (a) I. A. Levitsky, K. Kishikawa, S. H. Eichhorn and T. M. Swager, *J. Am. Chem. Soc.*, 2000, **122**, 2474-2479; (b) P. K. Jain, S. Eustis and M. A. El-Sayed, *J. Phys. Chem. B*, 2006, **110**, 18243-18253; (c) N. T. Fofang, T.-H. Park, O. Neumann, N. A. Mirin, P. Nordlander and N. J. Halas, *Nano Lett.*, 2008, **8**, 3481-3487.

26 For J-aggregates to occur, the ethynylene-linked oligomers necessarily exhibit slipped stacking motifs, with the sliding direction, or at the least a component of the sliding vector, parallel to the molecular transition dipole moment. The butadiynylene-linked oligomers presumably adopt analogous packing motifs. Such aggregate structures are consistent with previously studied PDI aggregation systems. (a) Baram, H. Weissman, Y. Tidhar, I. Pinkas and B. Rybtchinski, *Angew. Chem. Int. Ed*., 2014, **53**, 4123-4126; (b) C. Shahar, J. Baram, Y. Tidhar, H. Weissman, S. R. Cohen, I. Pinkas and B. Rybtchinski, *Acs Nano*, 2013, **7**, 3547-3556.