2D Supramolecular Polymers

DOI: 10.1002/anie.201307029

Formation of Two-Dimensional Supramolecular Polymers by Amphiphilic Pyrene Oligomers**

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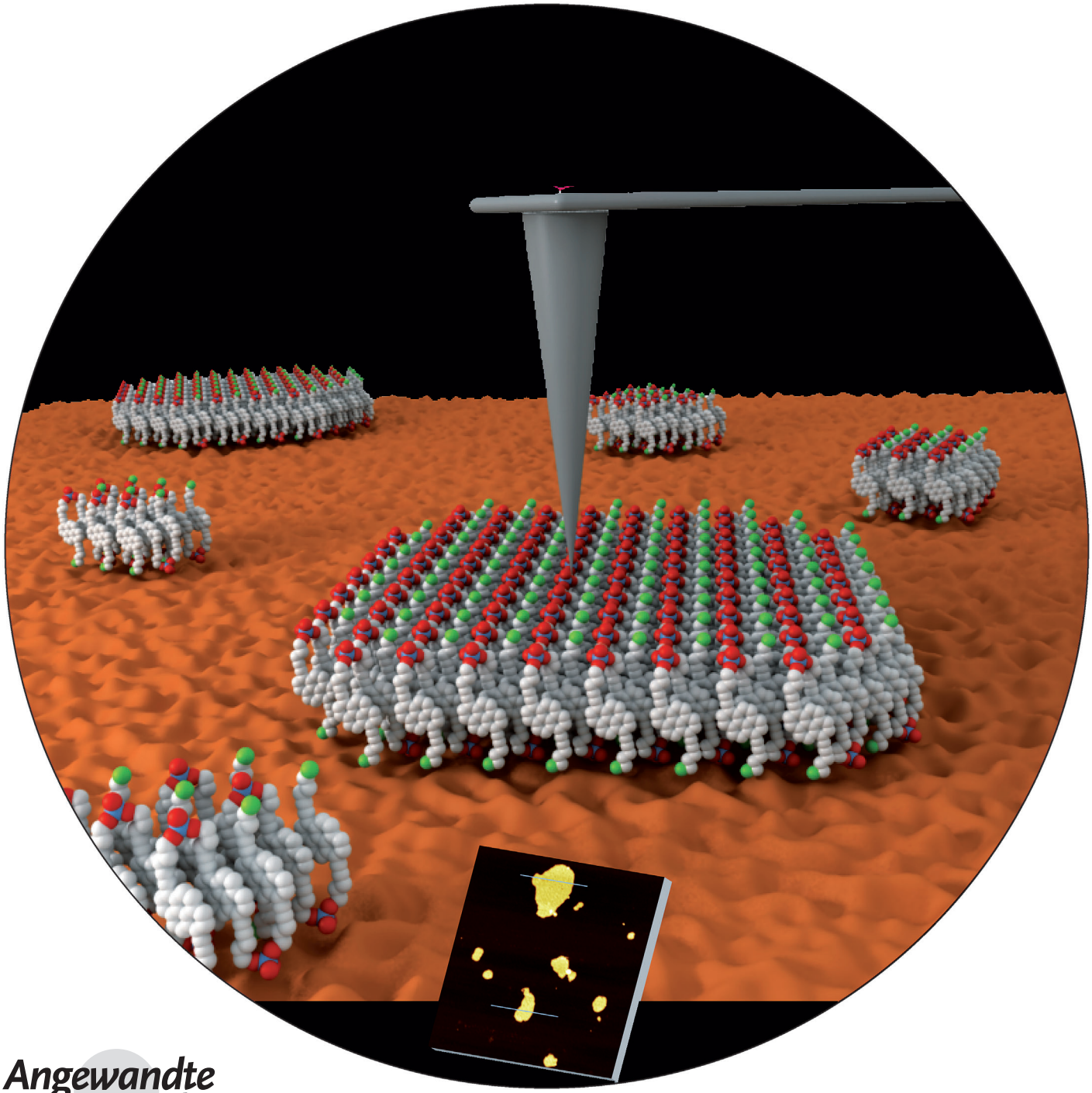
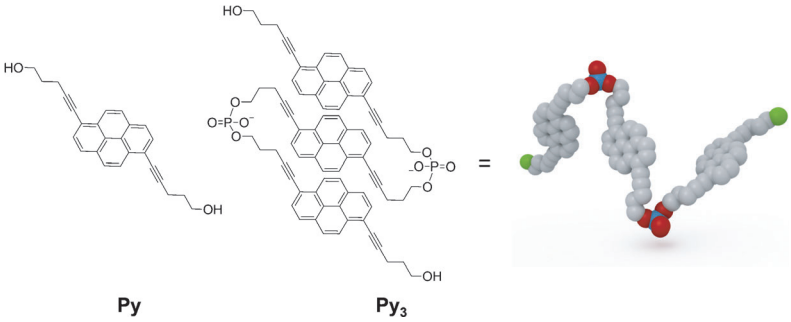


Organic π-conjugated molecules are attractive objects in the materials sciences.[1–8] The properties of dye aggregates critically depend on the degree of structural order. Control of the precise arrangement of chromophores into dimensionally and morphologically defined shapes is a key aspect in the development of optoelectronic devices.[9–17] Close spatial proximity and in-plane alignment of chromophores in 2D structural motifs[18–27] often results in distinct electronic interactions between the partners[28–36] leading to charge separation and transport, directional energy transfer, new optical and photophysical properties not observed in the separate molecules.[37–46] Moreover, spectroscopic changes often provide valuable information about the relative orientation of adjacent chromophores in a given environment.[39,47–50] Among the most prominent examples of electronic interactions with pronounced effects is the formation of J- and H-aggregates.[51–55] The type of aggregation strongly depends on the geometry and orientation of the interacting molecules as described by the theory of exciton coupling.[56,57]

Owing to their exceptional optical and electronic properties, pyrene derivatives find applications as chemical and biological sensors and labels, as components of dye-sensitized solar cells, in light-emitting diodes, or for photovoltaic applications.[58] Despite abundant information about its behavior in the aggregated state, data on J- and/or H-type interactions between pyrenes is very limited.[59,60] We investigate pyrene-modified nucleic acids as biosensors,[61] DNA-based light-harvesting[62,63] and energy-transfer systems[64] or as nanoscale templates for chromophore assembly.[65] Recently, a phosphodiester-linked pyrene heptamer (or heptapyrenotide[66]) was found to form rod-like structures by supramolecular polymerization.[67–69] Herein, we present the synthesis, the self-assembly behavior, morphological studies, and the spectroscopic properties of a phosphodiester linked, 1,6-dialkynyl-substitued pyrene trimer (**Py_3**, Scheme 1). This tripyrenotide exhibits solvent-dependent aggregation behavior that results in the formation of two-dimensional supramolecular polymers which is revealed by the unprecedented simultaneous occurrence of J- and H-type couplings for different electronic transitions.



Scheme 1. Structure of the phosphodiester-linked, 1,6-dipentinyl-substituted pyrene **Py** and the trimeric **Py_3**.

Synthesis of the 1,6-dipentynyl pyrene (**Py**, Scheme 1) followed reported procedures.[70] This derivative was further transformed into a suitably protected phosphoramidite building block and oligomerized by automated solid-phase synthesis. The trimer (**Py_3**) obtained was purified by size-exclusion chromatography and characterized by mass spectrometry (see Supporting Information).

The absorption spectrum of **Py_3** in ethanol (Figure 1) shows the first electronic transition in the range from 330–400 nm. A ratio of the intensities of the vibronic bands

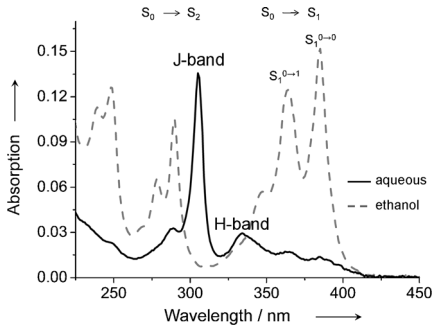


Figure 1. UV/Vis spectra of **Py_3** (1 μM) in ethanol (broken line) and in aqueous medium (10 mM sodium phosphate buffer, pH 7.2, 10 mM sodium chloride, ethanol 10 vol%, 20 °C).

$S_1^{0\rightarrow0}/S_1^{0\rightarrow1} = 1.2$ is observed. In aqueous medium several significant changes occur. 1) the ratio of the intensities $S_1^{0\rightarrow0}/S_1^{0\rightarrow1}$ decreases to 0.8, which shows a high degree of pyrene aggregation.[70,71] 2) the intensity of the $S_0\rightarrow S_1$ transition decreases dramatically and a new blue-shifted band with a $\lambda_{max} = 335$ nm appears (specified as H-band). 3) the $S_0\rightarrow S_2$ signals that were observed in ethanol mostly disappear. Instead, an intense, narrow and red-shifted band at $\lambda_{max} = 305$ nm (J-band) arises. These changes suggest that **Py_3** units are involved in a self-assembly process in aqueous medium leading to supramolecular polymers (SPs).[4,72–77] Evidence for the formation of aggregates of **Py_3** was provided by dynamic light scattering (DLS) experiments (Figure S9) indicating a medium particle size of 150–200 nm at 20 °C. The presence of a small amount of alcohol (10% ethanol was used routinely) is required to ensure the reversibility of the assembly/disassembly process.

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[**] Financial support by the Swiss National Foundation (grant 200020-132581, R.H.) and by the KTI (Project 13696.1, T.W.) are gratefully acknowledged. We thank Vyborna Yuliia for her contribution to the Frontispiece.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307029.

The formation of supramolecular polymers was unambiguously confirmed by AFM experiments. Since oligopyrenotides are structurally similar to DNA,[69] we followed the method developed for AFM investigations of DNA molecules.[78] Supramolecular assemblies were deposited on a mica surface modified with 3-aminopropyltriethoxy silane (APTES-mica) from a chosen sample solution (see Supporting Information for details). A representative AFM image is shown in Figure 2. It displays clearly distinguishable, free-standing 2D objects, like nanosheets. The AFM results with

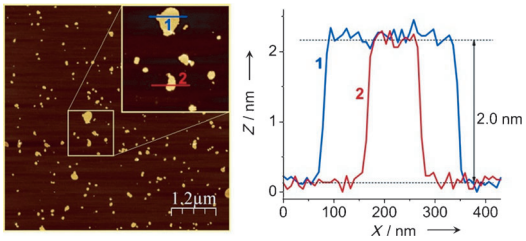


Figure 2. Left: Tapping-mode AFM images of 2D supramolecular polymers $(\mathbf{Py_3})_n$ deposited on APTES-mica from aqueous solution of $\mathbf{Py_3}$ containing 10% methanol. Right: typical cross-sections of two nanosheets along the lines shown in the inset of the AFM image.

APTES-mica as a substrate were highly reproducible. We detected nanosheets of 50–250 nm lateral size as deposited from the sample solutions (Figures S11, S12). The nanosheets have a rigid structure, as multiple AFM imaging of the same area did not lead to any morphological changes of the assemblies.

The self-assembly process was further studied by temperature-dependent experiments (Figure 3). Heating to 80 °C disrupts the structure of the SPs and J- and H-bands disappear concurrently. Intramolecular folding of pyrenes in $\mathbf{Py_3}$ is supported by the ratio $S_1^{0\rightarrow0}/S_1^{0\rightarrow1} = 0.8$. Cooling of the

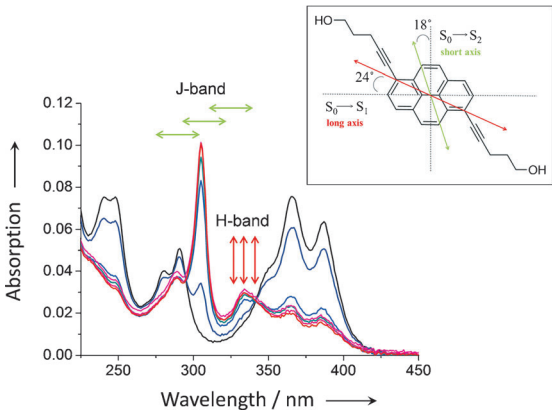


Figure 3. Temperature-dependent UV/Vis absorption spectra of $\mathbf{Py_3}$ in aqueous medium (conditions see Figure 1; equilibration was allowed for 20 min at each temperature). Red 20 °C, black 80 °C. Double-headed arrows illustrate the relative orientations of the electronic transition dipole moments. Inset: Orientation of the electronic transition dipole moments (red) in 1,6-dialkinyl pyrene (rotated by ca. 24° relative to the long and 18° to the short axis of unsubstituted pyrene, shown as dashed lines).

solution leads to the reappearance of the J- and H-bands. The positions of both, the J- and H-band, remain the same over the whole temperature range.

UV/Vis-monitored cooling curves (Figure 4) reveal a highly cooperative supramolecular polymerization process according to the nucleation-elongation model.[79,80] Absorp-

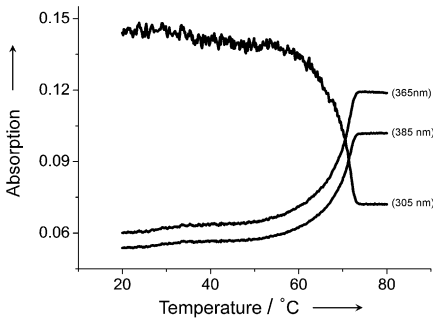
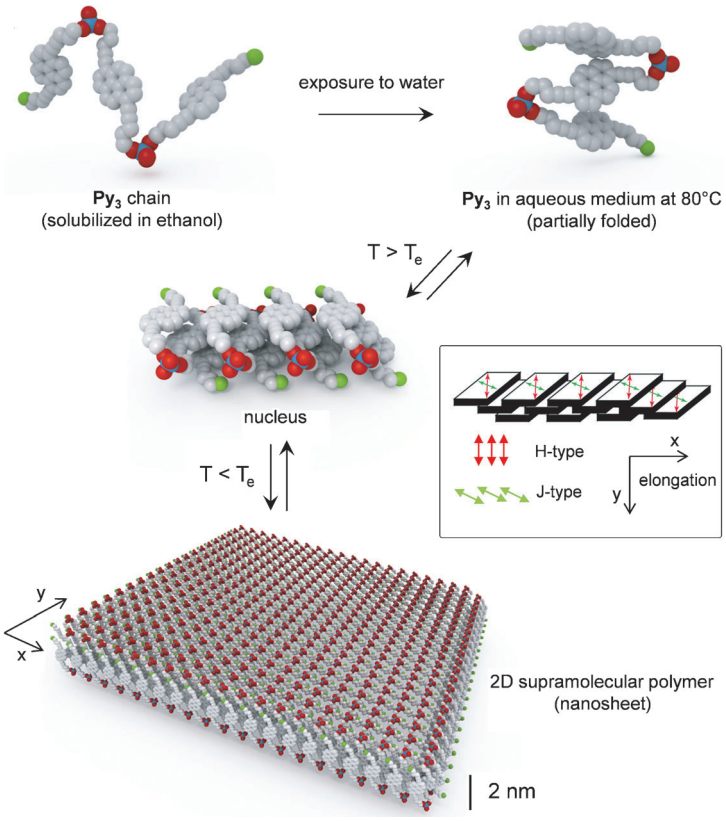


Figure 4. Supramolecular polymer formation curves (cooling rate 0.1 °C min^{-1}) recorded in aqueous medium (conditions as in Figure 1).

tion changes were recorded at three different wavelengths (305 nm, appearance of the J-band; 365 and 385 nm, vibronic bands of the first electronic transition). Evaluation of the curves according to the method by Schenning, Meijer, et al.[81] gives an elongation temperature (T_e) of 73 °C (Figure S10).

The observations can be rationalized by the formation of a two-dimensional supramolecular polymer (2DSP), as illustrated in Scheme 2. In ethanol, $\mathbf{Py_3}$ exists as random coils. The addition of water promotes intramolecular folding and formation of sheet-like supramolecular polymers. Within the supramolecular polymer, $\mathbf{Py_3}$ units are individually folded in a staircase-like manner which results in the proper alignment of the corresponding transition moments, as derived from the appearance of J- and H-bands in the UV/Vis spectra. Compared to unsubstituted pyrene, the introduction of the alkynyl linkers in the 1- and 6-position leads to a slight twisting of the orientation of the electronic transition dipole moments by approximately 24° relative to the long and 18° to the short axis of pyrene (see Figure 3, inset) caused by the interaction of the alkyne substituents with the π system; configuration interaction plays a less important role than in the unsubstituted pyrene because of the lower symmetry (see Figure S3).[82–84] The first intense electronic transition of **Py**, $S_0 \rightarrow S_1$, is of HOMO to LUMO type while some admixture HOMO−2, HOMO−1, and LUMO + 1, LUMO + 2 occurs in the intense $S_0 \rightarrow S_2$ transition. The oscillator strength of both transitions is large, which is important because exciton splitting is directly proportional to the oscillator strength (see for example, Eq. (1) in Ref. [49]). Folding of the amphiphilic $\mathbf{Py_3}$ in a staircase-like mode causes the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transition dipole moments to adopt an H- and a J-type orientation. To our knowledge, this is the first example of a multichromophore in which the first two electronic transitions are both very sensitive to excitonic coupling and lead to the simultaneous appearance of J- and H-type coupling. This is a different situation with respect to



Scheme 2. Illustration of 2D supramolecular polymerization. Amphiphilic **Py_3** units self-assemble in a temperature- and solvent-controlled process to form nano-sized sheets. The polymerization follows a nucleation-elongation pathway. Individual **Py_3** units are folded in a staircase-like fashion forming a hydrophobic pyrene layer (gray). Negatively charged phosphodiesters (red) are arranged on the outsides of the sheet.

the simultaneous occurrence of H- and J-coupling of degenerate states, known from porphyrins.[39,47,48]

The supramolecular polymerization process follows a nucleation-elongation pathway. The high degree of cooperativity may arise from the adoption of a defined staircase-like intramolecular fold of **Py_3** within the assemblies. This well-defined fold is absent at temperatures above. Once formed ($T = T_e$), the nucleus serves as a template that facilitates proper folding and assembly of additional **Py_3** units (elongation). The 2D polymeric structure further implies that the negatively charged phosphodiesters are arranged on the outsides of the nanosheet, while the pyrene units form a hydrophobic inner layer in an aqueous environment. AFM visualization demonstrates that the nanosheets have a highly uniform height of 2.0 ± 0.1 nm (Figure 2, right), which represents the thickness of the monolayer assembly (Scheme 2). The value is equal to the length of the long molecular axis of a phosphate-linked pyrene unit and, thus, in a good agreement with the proposed model.

Pyrenes form excimers when the association of two monomers is geometrically possible.[85–87] The most favorable geometry is a slightly slipped, sandwich-like orientation.[88] The fluorescence spectrum of **Py_3** in ethanol (Figure S5) shows a strong excimer signal ($\lambda_{max} = 509$ nm). In aqueous medium, at 20 °C however, **Py_3** exhibits predominantly monomer fluorescence (380–450 nm) and only very weak excimer emission (Figure 5). Upon heating, the excimer signal increases and at 80 °C it is the dominant band of the spectrum. This observation is consistent with a rigid two-dimensional structure at 20 °C, in which pyrene units are arranged at fixed positions and, hence, cannot adopt the sandwich-like arrangement of two pyrene units required for excimer formation. Residual excimer emission may originate from pyrene units located at the edges of the nanosheets, where the structure would be expected to be less rigid because of the dynamic nature of the supramolecular polymers. Increasing temperatures lead to dissociation of the aggregates and the higher flexibility of the pyrene units in separate trimeric units allows the formation of excimers. In addition, aggregation results in a general reduction of pyrene fluorescence. This is consistent with the quenching effect of H-aggregates.[89]

In conclusion, we have demonstrated that phosphodiester-linked trimers of a 1,6-dialkynyl-substituted pyrene behave as staircase-like foldamers, which cooperatively self-assemble into two-dimensional supramolecular polymers in aqueous medium. Folding and aggregation processes are accompanied by simultaneous development of J- and H-bands caused by the second and the first allowed electronic transitions, respectively, and significant changes in the fluorescence properties. In the amphiphilic sheet-like polymers, the negatively charged phosphodiester groups are arranged on the outsides of the layer formed by the hydrophobic pyrene units. The data

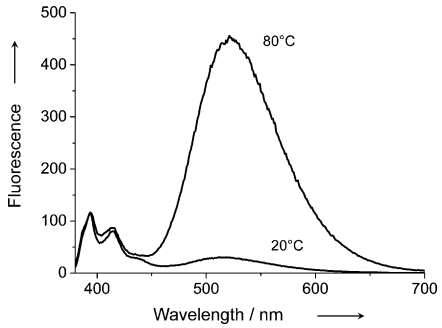


Figure 5. Fluorescence spectra of **Py_3** at 20 and 80 °C; excitation: 365 nm; conditions as in Figure 1; monomer: 380–450 nm; excimer: 450–700 nm.

presented herein differ significantly from findings with 1,8-disubstituted pyrene carboxamides, which give rise to quasi-one dimensional supramolecular polymers.[69,90] Effects of different linker types and substitution patterns are the topic of further investigations.

Received: August 9, 2013
Published online: September 25, 2013

Keywords: supramolecular polymers · H-aggregates · J-aggregates · nanosheets · pyrene

[1] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546.
[2] L. Zang, Y. Che, J. S. Moore, *Acc. Chem. Res.* **2008**, *41*, 1596 – 1608.
[3] Z. J. Chen, A. Lohr, C. R. Saha-Moller, F. Würthner, *Chem. Soc. Rev.* **2009**, *38*, 564 – 584.
[4] T. Aida, E. Meijer, S. I. Stupp, *Science* **2012**, *335*, 813 – 817.
[5] C. Li, M. Y. Liu, N. G. Pschirer, M. Baumgarten, K. Müllen, *Chem. Rev.* **2010**, *110*, 6817 – 6855.
[6] A. Geim, K. Novoselov, *Nat. Mater.* **2007**, *6*, 183 – 191.
[7] E. Orentas, M. Lista, N. T. Lin, N. Sakai, S. Matile, *Nat. Chem.* **2012**, *4*, 746 – 750.
[8] T. Fenske, H. G. Korth, A. Mohr, C. Schmuck, *Chem. Eur. J.* **2012**, *18*, 738 – 755.
[9] A. P. H. J. Schenning, E. W. Meijer, *Chem. Commun.* **2005**, 3245 – 3258.
[10] M. Muccini, *Nat. Mater.* **2006**, *5*, 605 – 613.
[11] E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72 – 196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72 – 191.
[12] S. Liu, W. M. Wang, A. L. Briseno, S. C. Mannsfeld, Z. Bao, *Adv. Mater.* **2009**, *21*, 1217 – 1232.
[13] T. F. A. de Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687 – 5754.
[14] K. Liu, C. Wang, Z. Li, X. Zhang, *Angew. Chem.* **2011**, *123*, 5054 – 5058; *Angew. Chem. Int. Ed.* **2011**, *50*, 4952 – 4956.
[15] Y. Chen, B. Zhu, Y. Han, Z. Bo, *J. Mater. Chem.* **2012**, *22*, 4927 – 4931.
[16] R. Nomura, R. Moriai, M. Kudo, T. Hoshino, J. Watanabe, S. Funyu, K. Ishitsuka, S. Okamoto, *J. Polym. Sci. Part A* **2013**, *51*, 3412 – 3419.
[17] S. S. Babu, S. Prasanthkumar, A. Ajayaghosh, *Angew. Chem.* **2012**, *124*, 1800 – 1810; *Angew. Chem. Int. Ed.* **2012**, *51*, 1766 – 1776.
[18] S. I. Stupp, S. Son, H. C. Lin, L. S. Li, *Science* **1993**, *259*, 59 – 63.
[19] S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384 – 389.
[20] J. Sakamoto, J. van Heijst, O. Lukin, A. D. Schlüter, *Angew. Chem.* **2009**, *121*, 1048 – 1089; *Angew. Chem. Int. Ed.* **2009**, *48*, 1030 – 1069.
[21] J. W. Colson, W. R. Dichtel, *Nat. Chem.* **2013**, *5*, 453 – 465.
[22] K. Baek, G. Yun, Y. Kim, D. Kim, R. Hota, I. Hwang, D. Xu, Y. H. Ko, G. H. Gu, J. H. Suh, C. G. Park, B. J. Sung, K. Kim, *J. Am. Chem. Soc.* **2013**, *135*, 6523 – 6528.
[23] Y. Anraku, A. Kishimura, Y. Yamasaki, K. Kataoka, *J. Am. Chem. Soc.* **2013**, *135*, 1423 – 1429.
[24] B. Narayan, S. P. Senanayak, A. Jain, K. Narayan, S. J. George, *Adv. Funct. Mater.* **2013**, *23*, 3053 – 3060.
[25] F. Li, Q. Song, L. Yang, G. Wu, X. Zhang, *Chem. Commun.* **2013**, *49*, 1808 – 1810.
[26] Y. Zheng, H. Zhou, D. Liu, G. Floudas, M. Wagner, K. Koynov, M. Mezger, H. J. Butt, T. Ikeda, *Angew. Chem.* **2013**, *125*, 4945 – 4948; *Angew. Chem. Int. Ed.* **2013**, *52*, 4845 – 4848.
[27] T. Govindaraju, M. B. Avinash, *Nanoscale* **2012**, *4*, 6102 – 6117.
[28] G. D. Scholes, G. Rumbles, *Nat. Mater.* **2006**, *5*, 683 – 696.
[29] G. D. Scholes, *ACS Nano* **2008**, *2*, 523 – 537.
[30] M. R. Wasielewski, *Acc. Chem. Res.* **2009**, *42*, 1910 – 1921.
[31] L. D. A. Siebbeles, F. C. Grozema, *Charge and Exciton Transport through Molecular Wires*, Wiley-VCH, Weinheim, **2011**.
[32] M. Porel, S. Jockusch, A. Parthasarathy, V. Rao, N. J. Turro, V. Ramamurthy, *Chem. Commun.* **2012**, *48*, 2710 – 2712.
[33] M. Han, Y. Okui, T. Hirade, *J. Mater. Chem. C* **2013**, *1*, 3448 – 3453.
[34] N. Sancho Oltra, W. R. Browne, G. Roelfes, *Chem. Eur. J.* **2013**, *19*, 2457 – 2461.
[35] V. Garg, G. Kodis, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, *J. Phys. Chem. B* **2013**, DOI: 10.1021/jp402265e.
[36] N. Yan, Z. Xu, K. K. Diehn, S. R. Raghavan, Y. Fang, R. G. Weiss, *Langmuir* **2013**, *29*, 793 – 805.
[37] F. C. De Schryver, T. Vosch, M. Cotlet, M. Van der Auweraer, K. Müllen, J. Hofkens, *Acc. Chem. Res.* **2005**, *38*, 514 – 522.
[38] G. Calzaferri, A. Devaux in *Supramolecular Photochemistry—Controlling Photochemical Processes*, (Eds.: V. Ramamurthy, Y. Inoue), Wiley, Hoboken, **2011**, pp. 285 – 387.
[39] *J-Aggregates* (Ed.: T. Kobayashi), World Scientific Publishing, Singapore, **2012**.
[40] Z. Zhao, J. W. Lam, B. Z. Tang, *J. Mater. Chem.* **2012**, *22*, 23726 – 23740.
[41] D. Görl, X. Zhang, F. Würthner, *Angew. Chem.* **2012**, *124*, 6434 – 6455; *Angew. Chem. Int. Ed.* **2012**, *51*, 6328 – 6348.
[42] P. D. Frischmann, K. Mahata, F. Würthner, *Chem. Soc. Rev.* **2013**, *42*, 1847 – 1870.
[43] D. Haldar, C. Schmuck, *Chem. Soc. Rev.* **2009**, *38*, 363 – 371.
[44] S. Prasanthkumar, A. Saeki, S. Seki, A. Ajayaghosh, *J. Am. Chem. Soc.* **2010**, *132*, 8866 – 8867.
[45] K. K. Kartha, S. S. Babu, S. Srinivasan, A. Ajayaghosh, *J. Am. Chem. Soc.* **2012**, *134*, 4834 – 4841.
[46] A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644 – 656.
[47] B. A. Friesen, K. R. Nishida, J. L. McHale, U. Mazur, *J. Phys. Chem. C* **2009**, *113*, 1709 – 1718.
[48] C. C. Rich, J. L. McHale, *J. Phys. Chem. C* **2013**, *117*, 10856 – 10865.
[49] G. Calzaferri, D. Brühwiler, T. Meng, L. Q. Dieu, V. L. Malinovskii, R. Häner, *Chem. Eur. J.* **2010**, *16*, 11289 – 11299.
[50] G. Sargsyan, A. A. Schatz, J. Kubelka, M. Balaz, *Chem. Commun.* **2013**, *49*, 1020 – 1022.
[51] E. E. Jelley, *Nature* **1936**, *138*, 1009 – 1010.
[52] G. Scheibe, *Angew. Chem.* **1936**, *49*, 563.
[53] M. Kasha, *Radiat. Res.* **1963**, *20*, 55 – 70.
[54] F. Würthner, T. E. Kaiser, C. R. Saha-Moeller, *Angew. Chem.* **2011**, *123*, 3436 – 3473; *Angew. Chem. Int. Ed.* **2011**, *50*, 3376 – 3410.
[55] D. Möbius, *Adv. Mater.* **1995**, *7*, 437 – 444.
[56] M. Kasha, H. R. Rawls, M. Ashraf El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371 – 392.
[57] S. E. Boiadjiev, D. A. Lightner, *Monatsh. Chem.* **2005**, *136*, 489 – 508.
[58] T. M. Figueira-Duarte, K. Müllen, *Chem. Rev.* **2011**, *111*, 7260 – 7314.
[59] D. Bhattacharjee, K. Mukherjee, T. N. Misra, *J. Phys. Chem. Solids* **2000**, *61*, 751 – 756.
[60] A. T. Haedler, H. Misslitz, C. Buehlmeyer, R. Q. Albuquerque, A. Köhler, H. W. Schmidt, *ChemPhysChem* **2013**, *14*, 1818 – 1829.
[61] S. M. Biner, D. Kummer, V. L. Malinovskii, R. Häner, *Org. Biomol. Chem.* **2011**, *9*, 2628 – 2633.
[62] O. O. Adeyemi, V. L. Malinovskii, S. M. Biner, G. Calzaferri, R. Häner, *Chem. Commun.* **2012**, *48*, 9589 – 9591.
[63] F. Garo, R. Häner, *Angew. Chem.* **2012**, *124*, 940 – 943; *Angew. Chem. Int. Ed.* **2012**, *51*, 916 – 919.
[64] F. Garo, R. Häner, *Bioconjugate Chem.* **2012**, *23*, 2105 – 2113.
[65] V. L. Malinovskii, A. L. Nussbaumer, R. Häner, *Angew. Chem.* **2012**, *124*, 4989 – 4992; *Angew. Chem. Int. Ed.* **2012**, *51*, 4905 – 4908.
[66] R. Häner, F. Garo, D. Wenger, V. L. Malinovskii, *J. Am. Chem. Soc.* **2010**, *132*, 7466 – 7471.
[67] A. L. Nussbaumer, D. Studer, V. L. Malinovskii, R. Häner, *Angew. Chem.* **2011**, *123*, 5604 – 5608; *Angew. Chem. Int. Ed.* **2011**, *50*, 5490 – 5494.

[68] A. L. Nussbaumer, F. Samain, V. L. Malinovskii, R. Häner, *Org. Biomol. Chem.* **2012**, *10*, 4891 – 4898.
[69] A. V. Rudnev, V. L. Malinovskii, A. L. Nussbaumer, A. Mishchenko, R. Häner, T. Wandlowski, *Macromolecules* **2012**, *45*, 5986 – 5992.
[70] H. Bittermann, D. Siegemund, V. L. Malinovskii, R. Häner, *J. Am. Chem. Soc.* **2008**, *130*, 15285 – 15287.
[71] W. Wang, L. S. Li, G. Helms, H. H. Zhou, A. D. Q. Li, *J. Am. Chem. Soc.* **2003**, *125*, 1120 – 1121.
[72] T. F. A. de Greef, E. W. Meijer, *Nature* **2008**, *453*, 171 – 173.
[73] J. M. Lehn, *Prog. Polym. Sci.* **2005**, *30*, 814 – 831.
[74] A. W. Bosman, R. P. Sijbesma, E. W. Meijer, *Mater. Today* **2004**, *7*, 34 – 39.
[75] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071 – 4097.
[76] J. S. Moore, *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 108 – 116.
[77] J. M. Lehn, *Angew. Chem.* **1990**, *102*, 1347 – 1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304 – 1319.
[78] Y. L. Lyubchenko, B. L. Jacobs, S. M. Lindsay, *Nucleic Acids Res.* **1992**, *20*, 3983 – 3986.
[79] P. A. Korevaar, S. J. George, A. J. Markvoort, M. M. Smulders, P. A. Hilbers, A. P. Schenning, T. F. De Greef, E. Meijer, *Nature* **2012**, *481*, 492 – 496.
[80] M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Chem. Eur. J.* **2010**, *16*, 362 – 367.
[81] P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Science* **2006**, *313*, 80 – 83.
[82] A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L. O. Palsson, D. J. Tozer, T. B. Marder, *J. Am. Chem. Soc.* **2011**, *133*, 13349 – 13362.
[83] T. Shyamala, S. Sankararaman, A. K. Mishra, *Chem. Phys.* **2006**, *330*, 469 – 477.
[84] C. Lambert, J. Ehbets, D. Rausch, M. Steeger, *J. Org. Chem.* **2012**, *77*, 6147 – 6154.
[85] F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587 – 614.
[86] F. C. De Schryver, P. Collart, J. Vandendriessche, R. Goedeweeck, A. M. Swinnen, M. Van der Auweraer, *Acc. Chem. Res.* **1987**, *20*, 159 – 166.
[87] K. Zachariasse, W. Kuhnle, *Z. Phys. Chem.* **1976**, *101*, 267 – 276.
[88] A. Warshel, E. Huler, *Chem. Phys.* **1974**, *6*, 463 – 468.
[89] U. Rösch, S. Yao, R. Wortmann, F. Würthner, *Angew. Chem.* **2006**, *118*, 7184 – 7188; *Angew. Chem. Int. Ed.* **2006**, *45*, 7026 – 7030.
[90] F. Simona, A. L. Nussbaumer, R. Häner, M. Cascella, *J. Phys. Chem. B* **2013**, *117*, 2576 – 2585.

