Fluorescence Memory

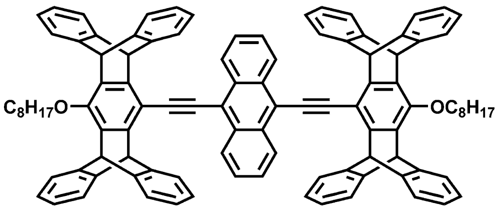
Deutsche Ausgabe: DOI: 10.1002/ange.201503406
Internationale Ausgabe: DOI: 10.1002/anie.201503406

Multicolor Fluorescence Writing Based on Host–Guest Interactions and Force-Induced Fluorescence-Color Memory**

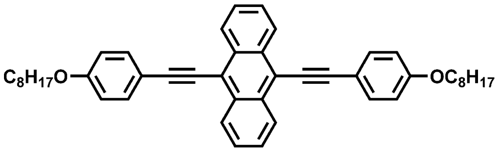
*Yuki Matsunaga and Jye-Shane Yang**

Abstract: *A new strategy is reported for multicolor fluorescence writing on thin solid films with mechanical forces. This concept is illustrated by the use of a green-fluorescent pentiptycene derivative* ***1****, which forms variably colored fluorescent exciplexes: a change from yellow to red was observed with anilines, and fluorescence quenching (a change to black) occurred in the presence of benzoquinone. Mechanical forces, such as grinding and shearing, induced a crystalline-to-amorphous phase transition in both the pristine and guest-adsorbed solids that led to a change in the fluorescence color (mechanofluorochromism) and a memory of the resulting color. Fluorescence drawings of five or more colors were created on glass or paper and could be readily erased by exposure to air and dichloromethane fumes. The structural and mechanistic aspects of the observations are also discussed.*

Smart materials undergo reversible changes in their properties in response to external stimuli. A new type of smart materials that display mechano-, vapo-, and/or thermofluorochromism in the solid or liquid-crystalline phase has recently emerged: Their fluorescence color and intensity are altered by mechanical forces, such as grinding, pressing, and shearing, but the initial state can be recovered by annealing and/or exposure to vapors of organic compounds or even water.[1,2] The mechanofluorochromic (MFC) behavior has been attributed to force-induced changes in intermolecular interactions as a result of either a (liquid-)crystalline-to-(liquid-)crystalline or crystalline-to-amorphous phase transition. As compared to dichromic MFC systems, the multicolor counterparts[3–5] have enhanced color contrast and patterning, which is beneficial for applications in sensors, displays, security printing, and data-storage devices. However, MFC systems that enable multicolor fluorescence writing or drawing as well as switching are rare; previous examples based on polymorphic[4] or bichromophoric[5] systems display up to three colors but require the careful control of temperature or mechanical forces. We report herein a new strategy toward multicolor fluorescence writing, in which a single chromophore is sufficient and the fluorescence color tuning is performed by guest molecules through host–guest interactions and exciplex formation at ambient temperature. This approach is demonstrated with the pentiptycene-derived 9,10-bis(phenylethynyl)anthracene **1** by the drawing of an apple, an orange, and a banana on a thin film of **1** on glass or paper (Figure 1; see also Figures S1–S3 in the Supporting Information). The important role of the pentiptycene scaffold in the observed multicolor fluorescence writing is evidenced by comparison with the pentiptycene-free planar analogue **2**.



1



2

The design of **1** as a guest-responsive MFC material relies on the prevention of compact intermolecular π stacking of the π-conjugated systems by the rigid bulky H-shaped pentiptycene scaffold[6] in the solid state, so that aggregation-induced fluorescence quenching is minimized and pore volumes accessible to guest molecules are created.[7,8] We also expected that a loose crystalline packing might facilitate the occurrence of force-induced phase transitions and thus the

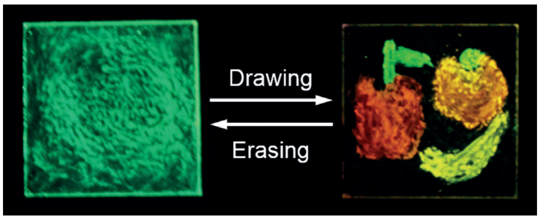


Figure 1. Multicolor fluorescence drawing of an apple, an orange, and a banana on a thin powder film of **1** on glass. The drawing was made by sequential sketching with a spatula and by fuming with the vapors of anilines DMA, DFDMA, and pMDMA and benzoquinone. The drawing was erased by blowing with air, followed by DCM fuming. See Figure S1 for detailed drawing procedures.

---

[*] Dr. Y. Matsunaga, Prof. J.-S. Yang
Department of Chemistry, National Taiwan University
No. 1 Sec. 4 Roosevelt Road, Taipei, 10617 (Taiwan)
E-mail: jsyang@ntu.edu.tw

[**] We thank the Ministry of Science and Technology (MOST) of Taiwan and National Taiwan University (NTU-ERP-104R891303) for financial support and Chih-Cheng Chang for assistance with PXRD measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503406.

MFC behavior. Indeed, the as-prepared solid **1** formed fluorescent exciplexes with a series of aniline derivatives with a fluorescence color ranging from greenish yellow to reddish orange. A "black" color was also created by fuming with benzoquinone because of fluorescence quenching. More importantly, mechanical forces not only cause a crystalline-to-amorphous phase transition in both the pristine and guest-adsorbed solids, thus leading to the MFC properties, but also impose a "memory" of the resulting color, which is the key for multicolor fluorescence writing.

Compounds **1** and **2** were readily synthesized through Sonogashira coupling reactions with commercially available 9,10-dibromoanthracene and the known building blocks ethynylpentiptycene[8] and ethynylbenzene[9] (see the Supporting Information for detailed synthetic procedures and compound characterization data). The pristine solid **1** showed a grinding-induced change in the color of fluorescence from green (G-form) to yellowish green (YG-form) with fluorescence maxima (λ_{fl}) at 506 and 540 nm, respectively (Figure 2a). Reversion from the YG- to the G-form was possible by fuming with dichloromethane (DCM) vapors. The fluorescence profile of the G-form resembles that in a dilute solution in DCM, thus indicating weak chromophore–chromophore interactions in the solid state. A redshift of 10 nm in the λ_{fl} value of the G-form relative to that in a dilute solution in DCM might result from the weak intermolecular interactions or simply from reabsorption of the short-wavelength emission under optically dense conditions.[8a] In contrast, the fluorescence profile of the YG-form differs from that of dilute solutions in DCM to a significant extent, thus indicating increased interactions between adjacent molecules. As the formation of fully sandwiched excimers is ruled out by the nonplanar bulky pentiptycene units, the YG-form is attributed to the formation of partially overlapped anthracene dimers and excimers (Figure 2b). This hypothesis is in part supported by the redshifted excitation spectrum (see Figure S4) and the longer fluorescence lifetime for the YG- (3.8 ns) versus the G-form (1.2 ns). Powder X-ray diffraction (PXRD) analysis indicated an amorphous structure for the ground samples (see Figure S5). The system is robust and showed no fatigue after several switching cycles between the G- and YG-forms (see Figure S6).

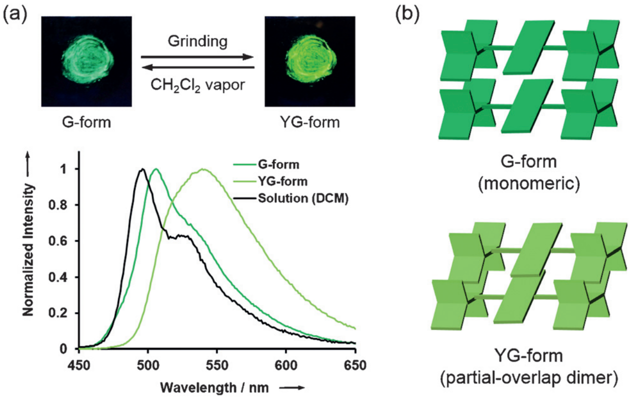


Figure 2. a) Photographs showing the reversible MFC behavior of **1** upon grinding and fuming with a solvent, and fluorescence spectra of **1** in the G- and YG-forms and as a solution in DCM. b) Schematic illustration of possible molecular arrangements in the G- and YG-forms.

The exciplex-based vapofluorochromic properties of **1** were investigated with electron-deficient benzoquinone (BQ) and electron-rich anilines with different substituents, including DMA, DEA, DIPA, DFDMA, and pMDMA (Figure 3). Whereas the solid-state fluorescence was quenched (black form) by BQ (see Figure S7), as attributed to photoinduced electron transfer from the host to the guest,[7] new emission attributable to exciplex formation (aniline·**1**) was observed with the aniline derivatives (Figure 3a). The ability of **1** to form exciplexes with anilines was supported by a titration experiment in solutions with DMA (see Figure S8). A broad emission band located at approximately 650 nm with a long decay time of 40 ns appeared in toluene but not in more polar solutions in THF and DCM: behavior typical of intermolecular exciplexes.[10] Interestingly, the color of the exciplex emission depended on the aniline and was brownish orange (BO-form), brownish yellow (BY-form), pale green (PG-form), greenish yellow (GY-form), and brownish red (BR-form) with DMA, DEA, DIPA, DFDMA, and pMDMA, respectively. The λ_{fl} value of aniline·**1** follows the order pMDMA·**1** (614 nm) > DMA·**1** (603 nm) > DEA·**1** (591 nm) > DIPA·**1** (577 nm) > DFDMA·**1** (572 nm), which reveals that aniline serves as the electron donor and **1** as the acceptor. The relatively smaller spectral shifts induced by DFDMA and DIPA could be attributed to their lower electron-donating ability as a result of the presence of electron-withdrawing F atoms and bulky *N*-isopropyl groups, respectively. The larger spectral shift induced by pMDMA relative to that observed with DMA is consistent

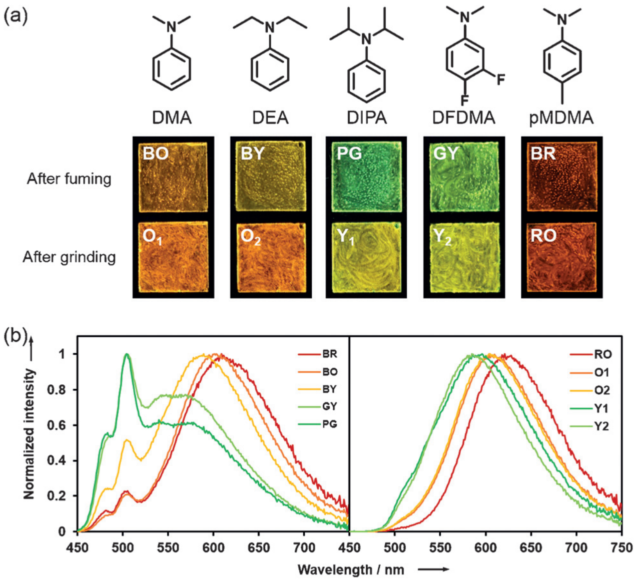


Figure 3. Fluorescence response of **1** to anilines. a) Photographs of aniline·**1** formed by fuming the G-form with aniline vapors for 10 min (top) and after grinding (bottom). b) The corresponding fluorescence spectra before (left) and after grinding (right).

with the presence of an additional electron-donating methyl group. Therefore, **1** is a potential fluorescent probe for the differentiation of structurally similar anilines. The overall shift in λ_{fl} on going from the G-form to the BR-form was as large as about 108 nm. Examples of solid-state exciplex formation with organic vapors are extremely rare,[11] and no example involving pentiptycene derivatives has been reported previously. Furthermore, this vapofluorochromism based on a host–guest interaction differs from the dichloromethane-vapor-induced YG-→G-form reversion, which is essentially a "recrystallization" mechanism.

The aniline·**1** complexes also displayed MFC behavior, albeit to a smaller extent than **1**. The grinding processes turned the BO- and BY-forms a brighter orange (O_1- and O_2-forms, respectively), the PG- and GY-forms yellow (Y_1- and Y_2-forms, respectively), and the BR-form reddish orange (RO-form; Figure 3a). The monomer emission nearly disappeared and the exciplex fluorescence was redshifted by 6–18 nm upon grinding (Figure 3b). Furthermore, except for the case of the GY→Y_2 transition, which led to a 50% decrease in fluorescence, the ground samples generally displayed a larger fluorescence quantum yield (up to 77% enhancement) than the unground samples (see Table S1 in the Supporting Information). Despite the changes in fluorescence intensity and the solid phase (see Figure S5), there was no significant variation in the exciplex fluorescence decay times for the ground versus unground samples. Evidently, the grinding process did not squeeze out the guest molecules but enhanced the host–guest interactions and/or the energy-transfer efficiency from the excited host molecule to the exciplex.

An unexpected but more important finding of this study is the distinct responsivity of ground and unground samples to vapor stimuli. For example, upon exposure to BQ vapors, the fluorescence of the G-form was completely quenched in 2 min, but residual fluorescence of the YG-form remained even after 10 min (Figure 4). A difference in responsivity between the G- and YG-forms was also observed with aniline vapors (Figure 4; see also Figure S9). This force-induced resistance to new vapor stimuli was persistent in the aniline·**1** complexes (Figure 4; see also Figure S10). For example, the fluorescence of the BO-form was completely quenched by BQ within 1 min, but the fluorescence quenching remained incomplete for the O_1-form after 3 min. The phenomenon of decreased fluorescence responsivity of ground samples to new guest molecules resembles a memory process caused by mechanical forces. We refer to this phenomenon of force-induced fluorescence-color memory as "mechanofluoromemory" (MFM). The responsivity to BQ was enhanced for aniline·**1** exciplexes relative to that of the pristine solid form of **1**, thus revealing that the previous exposure of unground samples to fumed guest molecules affects their responsivity to subsequent vapor stimuli. According to PXRD, the crystallinity of **1** was retained after fuming with anilines, although minor structural changes had occurred (see Figure S5). Such minor structural changes might facilitate the diffusion of BQ. Furthermore, the potential donor–acceptor (D–A) interactions between anilines and BQ might hold volatile BQ more effectively in **1** after fuming with an aniline derivative than in the pristine solid.

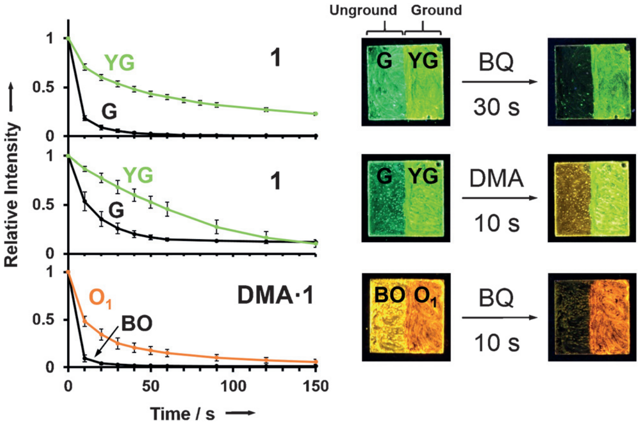


Figure 4. Comparison of fluorescence responsivity to guest molecules for ground and unground samples of **1** (G- and YG-forms) and DMA·**1** (BO- and O_1-forms) along with the corresponding plots of fluorescence intensity against the exposure time to the guest molecules. Fluorescence intensity was monitored at 506 nm for **1**, and at 603 and 609 nm for DMA·**1**.

The MFM properties of **1** provide a unique platform for multicolor fluorescence drawings. An apple, an orange, and a banana were sketched with a spatula on a thin powder film of **1** spread on glass (Figure 1; see also Figure S1) or on a filter paper containing **1** (see Figure S2). The drawing sequence started with the "leaves" (G-→YG-form) followed by the "orange" (BO-→O_1-form), the "banana" (GY-→Y_2-form), and the "apple" (BR-→RO-form), and ended by turning the background black by fuming with BQ. The fuming time for each guest vapor was approximately 10 s, and the time used for each element in the drawing was about 20–30 s. The drawing must be done soon after fuming with the guest, or the extent of color change is diminished, thus indicating a fast dissociation of the exciplex components in the open air. The drawing on glass resembles an oil painting, and the one on paper is more like a pastel painting. The drawings could be readily erased by blowing air over them, followed by fuming with DCM, and the recycled films behaved similarly (see Figure S3).

To gain insight into the observed MFM of **1**, we performed HPLC and fluorescence spectroscopic analysis of the spots of different colors in Figure 1. Whereas the emission color and the corresponding fluorescence spectra (see Figure S12) of the drawing spots closely resembled those of the pure forms shown in Figure 3, the HPLC results showed that all spots contained all three anilines used for fuming (DMA, DFDMA, and pMDMA), although the writing process did enhance the trapping of the aniline derivative that had been used in the last fuming step (see Figure S11 and Table S2). Evidently, not all host–guest interactions led to fluorescence signaling. We propose that there are two distinct types of host–guest interaction sites in the host: one could generate exciplex emission (exciplex-active sites), but the other is exciplex silent (exciplex-inactive sites) upon binding with anilines. The former sites allow fast diffusion and exchange of guests, but the latter sites are "stickier", and guest exchange at these sites is relatively slow.[12] Consequently, the exciplex-active sites are occupied mainly by the guests to which they have just been exposed, but the inactive sites would accumulate all the guests in the fuming history. The grinding processes change the phase from crystalline to amorphous. They therefore diminish the exciplex-active sites for new guests, confine the guests that previously occupied the exciplex-active sites (i.e., slow exchange with the new guests), and thus cause the fluorescence color to be memorized. The molar ratio of aniline molecules relative to **1**, as estimated by HPLC, was low (ca. 5–15 %; see Table S2) for all spots in the drawing, thus indicating that the exciplex concentration was rather low. This result in turn indicates that energy transfer from the intact host molecules or higher-lying exciplexes to lower-lying exciplexes is very efficient. Figure 5 summarizes the concept of MFM-based multicolor fluorescence writing schematically, but more studies are required for a firm conclusion to be reached on the MFM mechanism. In contrast, the amount of anilines detected by HPLC of the recycled thin films was negligible, thus indicating that the guest molecules were effectively removed during the recrystallization processes of DCM fuming.

The important role of the pentiptycene units in the MFC and MFM behavior of **1** was evidenced by comparison with the behavior of **2** under the same conditions. First, the size of the redshift in λ_{fl} on going from a dilute solution in DCM to the as-prepared solid was much larger for **2** than for **1** (64 versus 10 nm; see Table S3). Second, unlike for **1**, the change in the fluorescence color, intensity, and spectrum was small or negligible for the as-prepared solid **2** upon grinding or short-term fuming with the vapors of BQ or anilines (see Figures S13–S15). Both features indicate that **2** adopts a relatively compact crystal-packing mode with significant intermolecular π-stacking interactions and low pore volumes as compared to **1**. Another difference in the behavior of **1** and **2** is the opposite vapofluorochromicity of the ground versus unground samples. More specifically, ground samples of **2** displayed noticeable vapofluorochromicity to BQ and pMDMA upon prolonged fuming (10 min): 90 % of the fluorescence was quenched by BQ, and the fluorescence color was changed to orange by pMDMA; in contrast, only 15 % BQ-induced fluorescence quenching was observed and no change in the fluorescence color was observed for unground samples with pMDMA. It appears that grinding perturbs the ordered compact crystal packing of **2** and creates some disordered domains that correspond to nonideal active sites for interaction with guest molecules that are strong electron donors (i.e., pMDMA) or acceptors (i.e., BQ).

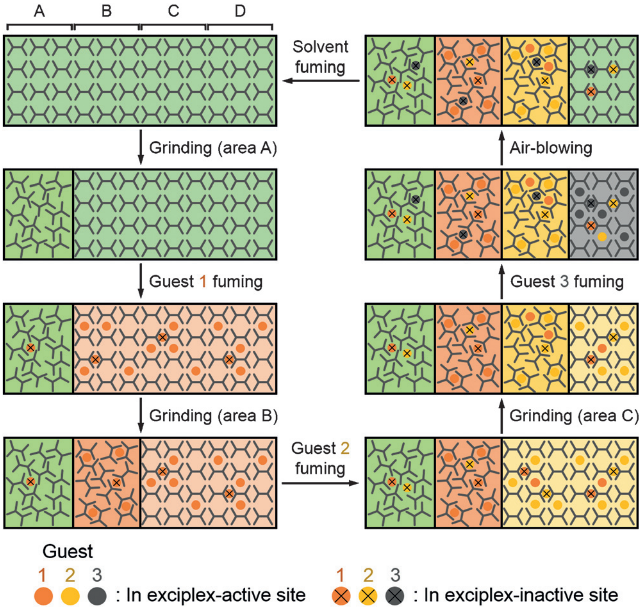


Figure 5. Schematic representation of the MFM-based multicolor fluorescence writing of **1** with guests 1–3. The crystalline phase contains both exciplex-active and exciplex-inactive sites for host–guest interactions. The diffusion of guest molecules into and out of the exciplex-active sites is fast, and exciplex formation changes the fluorescence color. In contrast, the diffusion of guest molecules into or out of the exciplex-inactive sites is slow, and the guest molecules are readily trapped in these sites. Nevertheless, these guests do not affect the fluorescence color. The grinding processes on areas A–C cause a crystalline-to-amorphous phase transition, which modifies the host–guest electronic interactions, diminishes the exciplex-active sites, traps the exciplex-forming guests, and causes retention of the fluorescence color prior to grinding. Blowing with air readily removes the guests in the unground area, and erasing of the writing is possible by solvent fuming to remove the trapped guest molecules and recrystallize the host.

In summary, the features of mechanofluoromemory and host–guest-interaction-based vapofluorochromism observed for the pentiptycene–anthracene π system **1** in the solid state demonstrate a new strategy toward multicolor fluorescence writing and switching. Mechanistically, the nonplanar bulky pentiptycene scaffold creates pores in the crystals with suitable volumes for ground-state host–guest interactions and excited-state exciplex formation or fluorescence quenching; however, mechanical forces change the molecular packing mode such that guest molecules are trapped in the exciplex-active sites and memorize the emission color. This strategy opens an avenue for the design of novel MFC smart materials for application in optical sensing and data storage.

Keywords: exciplexes · fluorescence · host–guest systems · mechanofluorochromism · vapochromism

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 7985–7989
Angew. Chem. **2015**, *127*, 8096–8100

---

[1] a) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* **2012**, *41*, 3878–3896; b) X. Zhang, Z. Chi, Y. Zhang, S. Liu, J. Xu, *J. Mater. Chem. C* **2013**, *1*, 3376–3390.

[2] a) H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 10044–10045; b) J. Wang, J. Mei, R. Hu, J. Z. Sun, A. Qin, B. Z. Tang, *J. Am. Chem. Soc.* **2012**, *134*, 9956–9966; c) Y. Sagara, T. Komatsu, T. Ueno, K. Hanaoka, T. Kato, T. Nagano, *Adv. Funct. Mater.* **2013**, *23*, 5277–5284.

[3] a) C. Dou, L. Han, S. Zhao, H. Zhang, Y. Wang, *J. Phys. Chem. Lett.* **2011**, *2*, 666–670; b) K. Nagura, S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y. Shimoikeda, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 10322–10325; c) P. Xue, P. Chen, J. Jia, Q. Xu, J. Sun, B. Yao, Z. Zhang, R. Lu, *Chem. Commun.* **2014**, *50*, 2569–2571; d) S. Yagai, S. Okamura, Y. Nakano, M. Yamauchi, K. Kishikawa, T. Karatsu, A. Kitamura, A. Ueno, D. Kuzuhara, H. Yamada, T. Seki, H. Ito, *Nat. Commun.* **2014**, *5*, 4013; e) Y. Zhang, K. Wang, G. Zhuang, Z. Xie, C. Zhang, F.

Cao, G. Pan, H. Chen, B. Zou, Y. Ma, *Chem. Eur. J.* **2015**, *21*, 2474 – 2479; f) T. Seki, T. Ozaki, T. Okura, K. Asakura, A. Sakon, H. Uekusa, H. Ito, *Chem. Sci.* **2015**, *6*, 2187 – 2195.

[4] Y. Sagara, T. Kato, *Angew. Chem. Int. Ed.* **2011**, *50*, 9128 – 9132; *Angew. Chem.* **2011**, *123*, 9294 – 9298.

[5] a) M.-J. Teng, X.-R. Jia, X.-F. Chen, Y. Wei, *Angew. Chem. Int. Ed.* **2012**, *51*, 6398 – 6401; *Angew. Chem.* **2012**, *124*, 6504 – 6507; b) Z. Ma, M. Teng, Z. Wang, S. Yang, X. Jia, *Angew. Chem. Int. Ed.* **2013**, *52*, 12268 – 12272; *Angew. Chem.* **2013**, *125*, 12494 – 12498; c) H.-J. Kim, D. R. Whang, J. Gierschner, C. H. Lee, S. Y. Park, *Angew. Chem. Int. Ed.* **2015**, *54*, 4330 – 4333; *Angew. Chem.* **2015**, *127*, 4404 – 4407.

[6] J.-S. Yang, J.-L. Yan, *Chem. Commun.* **2008**, 1501 – 1512.

[7] a) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 5321 – 5322; b) J.-S. Yang, T. M. Swager, *J. Am. Chem. Soc.* **1998**, *120*, 11864 – 11873.

[8] a) J.-S. Yang, J.-L. Yan, C.-Y. Hwang, S.-Y. Chiou, K.-L. Liau, H.-H. Gavin Tsai, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.* **2006**, *128*, 14109 – 14119; b) J.-S. Yang, J.-L. Yan, C.-K. Lin, C.-Y. Chen, Z.-Y. Xie, C.-H. Chen, *Angew. Chem. Int. Ed.* **2009**, *48*, 9936 – 9939; *Angew. Chem.* **2009**, *121*, 10120 – 10123.

[9] C.-J. Lin, C.-Y. Chen, S. K. Kundu, J.-S. Yang, *Inorg. Chem.* **2014**, *53*, 737 – 745.

[10] P. Kumar Bera, D. Nath, A. Misra, M. Chowdhury, *J. Photochem. Photobiol. A* **1996**, *95*, 127 – 136.

[11] a) Y. Takashima, V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nat. Commun.* **2011**, *2*, 168; b) Y. Kim, J. E. Whitten, T. M. Swager, *J. Am. Chem. Soc.* **2005**, *127*, 12122 – 12130.

[12] The exciplex-active and exciplex-inactive sites are probably associated with the planar anthracene ring and H-shaped pentiptycene peripheral rings, respectively.

Received: April 15, 2015