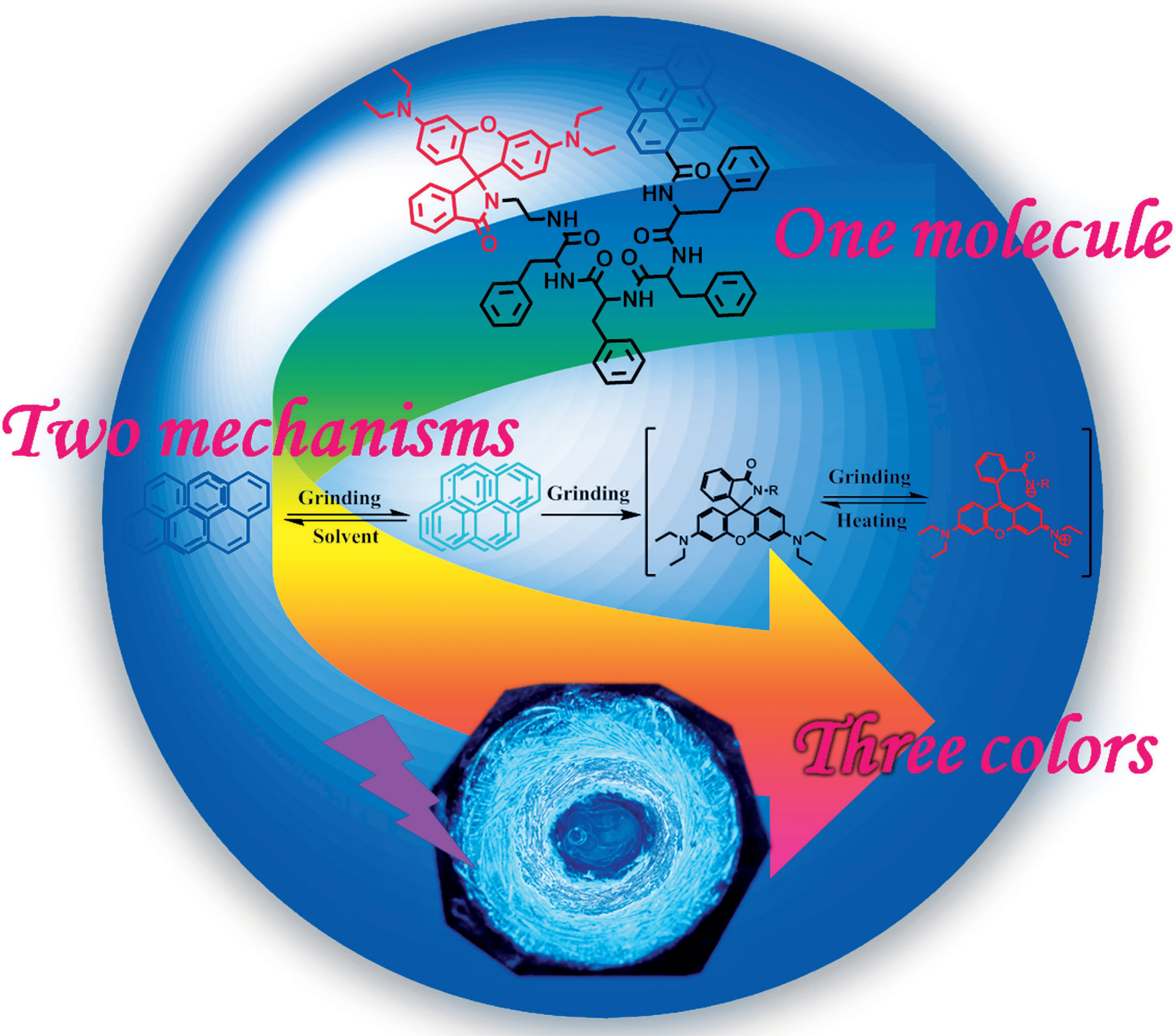
Mechanochromic Fluorescence

DOI: 10.1002/anie.201306503

Mechanically Induced Multicolor Switching Based on a Single Organic Molecule**

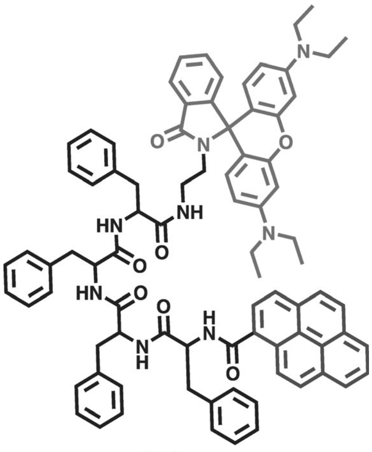
Zhiyong Ma, Mingjun Teng, Zhijian Wang, Shuang Yang, and Xinru Jia*



The development of multicolored switches that are triggered by a mechanical stimulus remains an interesting but challenging subject because such switches not only possesses significance in fundamental research but can also create new applications for luminescent materials.[1] To date, few examples of external-force-induced multicolored change, such as a three-color transition, have been reported.[2] One excellent example is the tricolored mechanochromic liquid crystal developed by Sagara and Kato.[2a] The liquid crystal was composed of a dumbbell-shaped compound and a dendronlike molecule but only a single luminophore. It showed reversible tricolored switching accompanied by different molecular-packing architectures. Previously, we reported a multicolored coaggregate whose color changed from blue to green and reddish in response to an external force. This color change was enabled by variation of the molecular assembly and ring opening of the spirolactam. The use of two available chromophores in this way broadens the range of possible preparation approaches to mechanical-response materials.[2b] However, multicolored emission and a switch that operates by modulation of the assembled structures of a single organic molecule by a force-induced reaction have not been described.

Motivated by the previous findings, we have been trying to design and synthesize a simple molecule with two different chromophores that could show three colors. The discovery of such a compound may increase our knowledge on the relationship between molecular structure and luminescence behavior and enable a molecular-design strategy to be established for the development of force-sensitive molecules. Moreover, such organic materials would have the advantages of well-defined structures, facile preparative methods, readily tunable properties, and high functionality.

Herein, we report a novel organic molecule **M-1** with tetraphenylalanine as a spacer to link the chromophores of pyrene and rhodamine B. Compound **M-1** could change color from blue to bluish-green and further to a reddish color. This color transition could be reversed by heating and treatment of the sample with solvents. Compound **M-1** is a rare example of a mechanochromic material composed of a single organic molecule. It is also unusual that its multicolored emission can be tuned simply by different packing of the chromophores and a force-induced ring-opening reaction.



M-1

Scheme 1. Structure of **M-1**.

The designed molecule **M-1** (Scheme 1) was synthesized from rhodamine B (the ring-opened form), which reacted with ethylenediamine to afford RhB-NH_2 as the corresponding spirolactam (see Scheme S1 in the Supporting Information). Standard coupling of RhB-NH_2 and *tert*-butoxycarbonyl (Boc)-protected phenylalanine (Phe) in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) was followed by removal of the Boc group with trifluoroacetic acid and triethylamine and then linking of the resultant intermediate to the Boc-protected Phe. In a second reaction cycle, removal of the Boc group was followed by coupling with Boc-protected Phe-Phe. Finally, removal of the Boc protecting group in the product and coupling with 1-pyrenecarboxylic acid gave the target molecule **M-1**. The structure of **M-1** with four phenylalanine residues, a pyrene unit, and a rhodamine B moiety is shown in Scheme 1. ^{1}H NMR and ^{13}C NMR spectroscopy as well as HRMS analysis were used to verify the structure and purity of **M-1**. The detailed synthetic procedures and characterization of **M-1** are described in the Supporting Information.

M-1 displayed reversible multicolored mechanochromic luminescent (ML) behavior. To observe the three colors more clearly, we distributed the sample smoothly on an agate mortar. It could be seen that the powder divided into different areas of color emission upon grinding: original blue (center ring), bluish-green (external ring), and reddish (middle ring; Figure 1 a). The blue color was fully recovered by heating the reddish powder at 120 °C for several minutes and then treating the sample with CH_2Cl_2 at room temperature (Figure 1 c; see also Figure S3).

Figure 1 b shows the fluorescence emission spectra of the powder before and after the application of an external force. The emission centered at 440 nm [$\Phi = 0.188$, $\tau_1 = 4.93$ ns ($A_1 = 00.34$), $\tau_2 = 22.17$ ns ($A_2 = 0.66$)] for the initial powder was red-shifted to 480 nm [$\Phi = 0.272$, $\tau_1 = 19.59$ ns ($A_1 = 00.49$), $\tau_2 = 64.84$ ns ($A_2 = 00.51$)] after grinding. After further force disturbance, a new peak at 583 nm was detected for the reddish powder. The emission appeared at 440 nm again when the reddish powder was heated and then treated with a solvent. According to pioneering studies[3] and our previous results,[2b,4] the emissions at 440 and 480 nm mainly originate from pyrene excimers: a partially overlapping excimer **I** with

---

[*] Z. Y. Ma, Dr. M. J. Teng, Z. J. Wang, S. Yang, Prof. X. R. Jia
Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871 (China)
E-mail: xrjia@pku.edu.cn

[**] This research was supported financially by the National Natural Science Foundation of China (21174005 to X.R.J.) and partially supported by the National Basic Research Program of China (973 Program, No. 2011CB933300). We thank Prof. X. H. Wan, H. Jiang, and E. Q. Chen for useful discussions and help with the experiments.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306503.

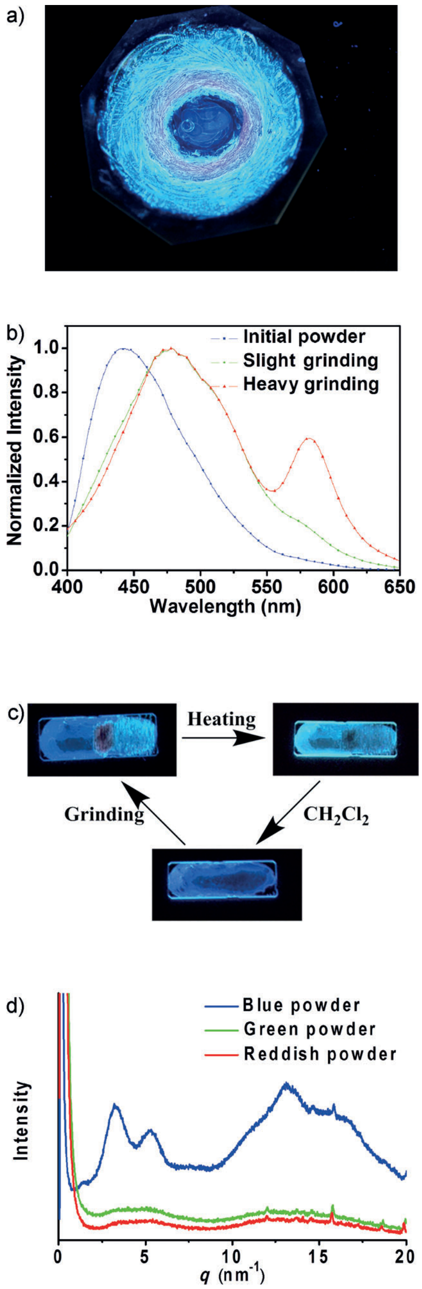


Figure 1. a) Different emission colors (upon irradiation with 365 nm UV light) of **M-1** on an agate mortar upon grinding: original blue (center), reddish (middle ring), and bluish-green (external ring). b) Fluorescence spectra of the initial powder and the same sample upon grinding ($\lambda_{ex}=365$ nm). c) Reversible change in the emission colors in situ. d) SAXS patterns of the blue powder (blue line), bluish-green powder (green line), and reddish powder (red line).

a short lifetime and low quantum yield, and a sandwich-packing excimer **II** with a long lifetime and high quantum yield, respectively. The reddish color of the sample was due to a force-induced chemical transformation of rhodamine B from a spirolactam into a ring-opened amide.

We used differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS) measurements to elucidate the microstructure of the initial powder (see Figures S4 and S5). A sharp endothermic peak was observed at 151.9 °C in the first heating cycle. However, it disappeared and was replaced by a glass-transition peak at 140.9 °C when the sample was ground. This change implies a transition from a possibly ordered structure in the initial powder to an amorphous phase in the ground powder. The scattering profile of SAXS showed two major diffraction peaks at the low angle with a scattering vector ratio of 1:$\sqrt{3}$. These peaks could be ascribed to a 100/110 reflection of a hexagonal columnar packing arrangement (Figure 1 d), but not to a perfectly ordered columnar arrangement owing to the broadness of the diffraction features. After slight grinding, the columnar array was disrupted, with the disappearance of the two diffraction peaks; further grinding afforded the reddish sample without any diffraction signals. These results indicated that the ground bluish-green or reddish powder was amorphous.

As the initial powder emitted a blue color at 440 nm, most of the pyrenyl groups were assumed to be partly overlapped with one another. We deduced a helical-like hexagonal columnar packing mode for the initial powder on the basis of a combination of the DSC and SAXS results (see Figure S6). In the columnar arrangement, the molecules were arranged with the pyrene groups on one side to match the partly overlapped packing pattern. The column diameter calculated by SAXS was 2.30 nm, which corresponds to the optimized geometry of **M-1** with a molecular length of 1.98 nm (see Figure S7). This deduction was further supported by circular dichroism (CD) measurements.[5] For the initial powder, a negative band at 288 nm and a broad band in the range of 345–376 nm were observed, in accordance with the absorption of the pyrenyl moieties (see Figure S8).[3b,d] To confirm the helical-like packing of the molecules in the initial powder, we recorded CD spectra of samples prepared by dissolving **M-1** in dichloromethane and then adding *n*-hexane dropwise to the resulting solution until a white precipitate formed. A strong signal due to the phenylalanine residues was observed at 266 nm for the dilute solution of **M-1**. However, when *n*-hexane was added dropwise to the solution, the signal at 288 nm and the broad band at 345–376 nm developed and increased gradually, thus indicating the establishment of ordered helical-like column packing of **M-1** in the precipitation process (Figure 2). Furthermore, in luminescence studies of solutions of **M-1** in mixtures of dichloromethane and hexane, the emission at 440 nm appeared as *n*-hexane was gradually added to the solution, thus indicating that aggregation also occurred in solution (see Figure S9).

Noncovalent interactions, such as hydrogen bonding of the amide groups and the π–π stacking of phenyl groups, may play key roles in the aggregated structure of the initial powder. We performed Fourier transform infrared (FTIR) spectroscopy to further confirm the self-assembled structure at the molecular level (see Figure S10). For the initial powder, the characteristic stretching absorption band of the hydrogen-bonded form of amide N−H groups was observed at 3274 cm^{-1}, which is considerably lower than the position of the absorption band for a free N−H group (ca. 3400 cm^{-1}). This band gradually grew weaker and became broader as the blue sample was converted into the bluish-green and then the

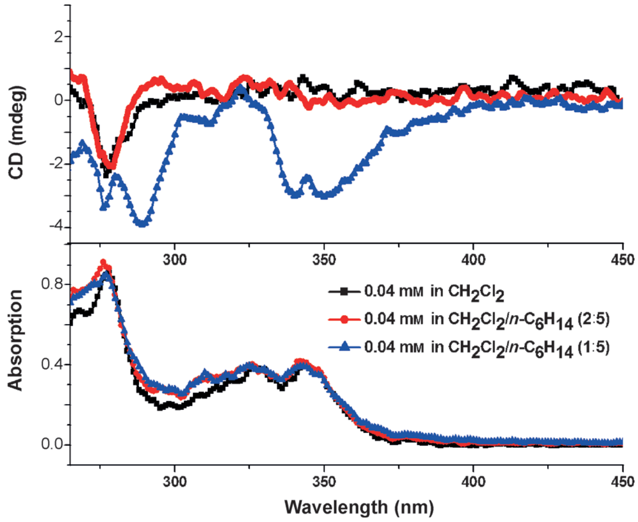


Figure 2. a) CD and b) UV/Vis spectra of the samples prepared by the dropwise addition of *n*-hexane to a solution of **M-1** in dichloromethane (solvent ratio: v/v).

reddish samples. This transformation of the FTIR spectrum indicates the increasing destruction of hydrogen bonds and the conversion from the ordered structure into the amorphous phase.

The ring-opening reaction of rhodamine B was characterized by UV/Vis and fluorescence spectroscopy. The reddish powder was dissolved in dichloromethane, and the resulting solution was compared to the solution of the initial powder in dichloromethane. New absorption and emission bands at 550 and 580 nm emerged in the UV (see Figure S11) and fluorescence spectra (see Figure S12), respectively, and were assigned to the maximum absorption and characteristic emission of the ring-opened rhodamine B species.

Rhodamine B is well-known for its ring-opening reaction, which occurs either in an acidic environment or upon complexation with metal cations through the activation of the carbonyl group in the spirolactam and leads to a strong fluorescence emission with a pink color.[6] We analyzed and estimated the approximate energy required to cleave the covalent bond between the spiro carbon atom and the amide nitrogen atom (marked as bond 1 in Figures S13–S16) in the spirolactam. The energy of this bond may provide insight into the mechanical reaction. We employed the COGEF method[7] to stimulate the bond 1 cleavage process and calculate the activation energy of fragmentation (see the Supporting Information). Bond 1 was found to be relatively weak and was broken when the energy was increased to 104, 100, and 105 kJ mol^{-1} at the selected three points of the N atom, the carbonyl O atom, and the spiro C atom, respectively. Thus, the minimum energy necessary for the force-induced ring-opening reaction is approximately 100 kJ mol^{-1} in our system.

The tricolored switching of **M-1** is molecular-structure dependent. The structure of the spacer is crucial for pyrene excimer formation. As reported, excimer **I** usually exists in a restricted environment in which a partially overlapped packing mode is adopted, such as in crystals and viscous liquids.[3] Hence, the ability to modulate the overlapped packing pattern of the pyrene excimer for blue emission is an important focus for the development of a multicolored switch in our case. In general, there is a color change between the two colors of bluish-green and reddish, but the blue color is missed. For example, with an amidoamine-based structure as the spacer, no formation of excimer **I** of pyrene was observed.[8] To gain further evidence of the role of tetraphenylalanine, we examined the mechanochromic properties of a 1:1 mixture of 1-pyrenecarboxylic acid and the Boc-protected intermediate in the synthesis of **M-1** that contained the tetraphenylalanine spacer and the rhodamine B moiety but not the pyrene chromophore (see Figure S17). It was found that the emission of the mixed powder was initially centered at 490 nm, and that another band at 580 nm appeared upon grinding. The different behavior from that of **M-1**, which shows the emission of excimer **I** at a lower wavelength, is due to two factors: 1) excimer **II** of pyrene is a more stable in the mixture owing to enhancement of the π–π interaction; and 2) the tetraphenylalanine spacer facilitates orderly packing of **M-1** in the initial powder; thus, the movement of pyrene groups is constrained, which leads to the formation of excimer **I** as partially overlapping packed dimeric units.

On the basis of the above results and analysis, the mechanically induced multicolored switching of **M-1** can be summarized as follows (see Figure S18): The initial powder of **M-1** emits blue luminescence (440 nm) because of the partially overlapped packing of excimer **I** in a helical-like hexagonal column. Upon slightly grinding, the assembled structures are destroyed, which leads to a sandwich stacking of the pyrene moieties and results in a change in fluorescence from blue to bluish-green. Extreme force perturbation induces the ring-opening reaction of rhodamine B from a spirolactam to a ring-opened amide with a reddish color. The emission switches from blue to bluish-green to reddish in sequence as the external force increases. However, quantification of the applied force to induce the color change is still pending[9] as an important and tough topic of the future research in our laboratory.

In summary, we have prepared a material composed of a single organic molecule that undergoes multicolored fluorescence switching by combining mechanisms of the force-induced transformation of assembled structures and chemical reactivity, that is, "one molecule, two mechanisms, three colors". The tetraphenylalanine spacer plays a crucial role in the formation of the aggregated architecture of the initial powder with its blue color. Owing to its straightforward synthesis, molecule **M-1** may have the potential for application in fluorescent sensors, security inks, and probes.

Received: July 25, 2013
Revised: September 24, 2013

Keywords: chromophores · excimers · mechanochromic fluorescence · ring opening · tricolored switches

[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) F. Ciardelli, G. Ruggeri, A. Pucci, *Chem. Soc. Rev.* **2013**, *42*, 857 – 870; c) Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605 – 610; d) Y. Chen, A. J. H. Spiering, S. Karthikeyan, G. W. M. Peters, E. W. Meijer, R. P. Sijbesma, *Nat. Chem.* **2012**, *4*, 559 – 562; e) X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo, B. Z. Tang, *Adv. Mater.* **2011**, *23*, 3261 – 3265; f) X. Luo, W. Zhao, J. Shi, C. Li, Z. Liu, Z. Bo, Y. Q. Dong, B. Z. Tang, *J. Phys. Chem. C* **2012**, *116*, 21967 – 21972; g) X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun, B. Z. Tang, *J. Phys. Chem. C* **2012**, *116*, 10541 – 10547; h) J. Wang, J. Mei, R. Hu, J. Z. Sun, A. Qin, B. Z. Tang, *J. Am. Chem. Soc.* **2012**, *134*, 9956 – 9966; i) S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2010**, *132*, 13675 – 13683; j) M. S. Kwon, J. Gierschner, S. J. Yoon, S. Y. Park, *Adv. Mater.* **2012**, *24*, 5401 – 5401; k) J. W. Chung, Y. You, H. S. Huh, B. K. An, S. J. Yoon, S. H. Kim, S. W. Lee, S. Y. Park, *J. Am. Chem. Soc.* **2009**, *131*, 8163 – 8172; l) X. Zhang, Z. Chi, B. Xu, L. Jiang, X. Zhou, Y. Zhang, S. Liu, J. Xu, *Chem. Commun.* **2012**, *48*, 10895-10897; m) Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou, W. Tian, *Angew. Chem.* **2012**, *124*, 10940 – 10943; *Angew. Chem. Int. Ed.* **2012**, *51*, 10782 – 10785; n) G. Zhang, J. Lu, M. Sabat, C. L. Fraser, *J. Am. Chem. Soc.* **2010**, *132*, 2160 – 2162.

[2] a) Y. Sagara, T. Kato, *Angew. Chem.* **2011**, *123*, 9294 – 9298; *Angew. Chem. Int. Ed.* **2011**, *50*, 9128 – 9132; b) M. J. Teng, X. R. Jia, X. F. Chen, Y. Wei, *Angew. Chem.* **2012**, *124*, 6504 – 6507; *Angew. Chem. Int. Ed.* **2012**, *51*, 6398 – 6401.

[3] a) J. B. Birks, *Rep. Prog. Phys.* **1975**, *38*, 903; b) F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587; c) Y. Tsujii, T. Itoh, T. Fukuda, T. Miyamoto, *Langmuir* **1992**, *8*, 936; d) F. M. Winnik, N. Tamai, J. Yonezawa, Y. Nishimura, I. Yamzaki, *J. Phys. Chem.* **1992**, *96*, 1967.

[4] a) M. J. Teng, X. R. Jia, S. Yang, X. F. Chen, Y. Wei, *Adv. Mater.* **2012**, *24*, 1255 – 1261; b) M. J. Teng, X. R. Jia, X. Chen, Z. Y. Ma, Y. Wei, *Chem. Commun.* **2011**, *47*, 6078 – 6080.

[5] a) Y. Kamikawa, T. Kato, *Langmuir* **2006**, *23*, 274 – 278; b) G. Liang, Z. Yang, R. Zhang, L. Li, Y. Fan, Y. Kuang, Y. Gao, T. Wang, W. W. Lu, B. Xu, *Langmuir* **2009**, *25*, 8419 – 8422.

[6] a) X. Chen, T. Pradhan, F. Wang, J. S. Kim, J. Yoon, *Chem. Rev.* **2011**, *112*, 1910 – 1956; b) S. Kang, S. Kim, Y.-K. Yang, S. Bae, J. Tae, *Tetrahedron Lett.* **2009**, *50*, 2010 – 2012.

[7] COGEF = constrained geometries simulate external force; a) D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore, N. R. Sottos, *Nature* **2009**, *459*, 68 – 72; b) J. K. Matthew, M. M. Alexander, J. S. Moore, *J. Am. Chem. Soc.* **2011**, *133*, 18992 – 18998.

[8] Z. Y. Ma, M. J. Teng, Z. J. Wang, X. R. Jia, *Tetrahedron Lett.*, DOI: 10.1016/j.tetlet.2013.09.083.

[9] K. Nagura, S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y. Shimoikeda, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 10322 – 10325.