Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Hui Tong [a], Yongqiang Dong [a], Matthias Häußler [a], Zhen Li [a], Baoxiu Mi [a], Hoi Sing Kwok [b] & Ben Zhong Tang [c d]

[a] Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

[b] Center for Display Research, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

[c] Department of Chemistry and Center for Display Research, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

[d] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China

Version of record first published: 16 Aug 2006

Mol. Cryst. Liq. Cryst., Vol. 446, pp. 183–191, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500374567

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Hui Tong
Yongqiang Dong
Matthias Häußler
Zhen Li
Baoxiu Mi
Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

Hoi Sing Kwok
Center for Display Research, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China

Ben Zhong Tang
Department of Chemistry and Center for Display Research, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China and Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China

A series of new linear and cyclic polyenes including siloles, butadienes, cyclcobutenes, fulvenes, and 4H-pyrans are designed and synthesized. When molecularly dissolved in common organic solvents, all the polyenes are practically nonemissive. Addition of poor solvents induces the polyenes to cluster into nanoaggregates, which turns the emission of the polyenes "on" and boosts their luminescence efficiencies dramatically (hence "aggregation-induced emission" or AIE). The emission color ranges from blue to red, depending on the chromophoric structures. Polyene nanoparticles on TLC plates show bright blue fluorescence which switches off reversibly in an atmosphere of volatile organic compounds. Addition of poor solvents to solution of cyclic polyenes bearing cholsteryl moieties leads to polarized green and anisotropic red emissions dependant on the solvent ratios. The different emissions may be caused by different packing patterns of the polyene crystals under different conditions.

Keywords: AIE; aggregation-induced-emission; polarized emission; polyene

Address correspondence to Ben Zhong Tang, Department of chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk

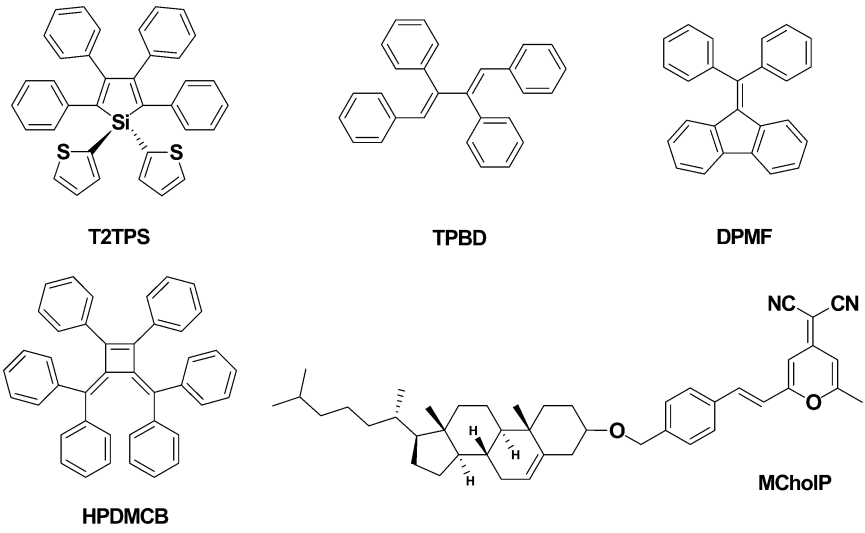
INTRODUCTION

Organic luminescence molecules have attracted considerable attention since the initial works on organic light-emitting devices (OLEDs) due to their potential applications in full-color flat-panel displays [1,2]. Despite humongous advances, the strong fluorescence exhibited by most organic dyes in their dilute solutions is quenched upon fabrication into thin films, which strongly limits the scope of their device applications [3,4]. This quenching effect is believed to be the result of aggregate or excimer formation, which leads to a reduction in the luminescence efficiency [5,6]. Many groups have tried to prevent aggregate formation in the solid states by separating the dye chromophores through the introduction of sterically hindered structures such as dendron substituents [7,8]. In fact, it would be more interesting to explore novel organic molecules or polymers, which not only do not suffer fluorescence quenching in the aggregated state, but display enhanced light emission in the solid state or in thin films. Some examples such as sterically crowded siloles [9,10], biphenyl substituted ethylenes [11] and diaminodicyanoquinodimethanes [12] have been reported to show stronger light emission in solid states than their dilute solutions.

In our previous work, we have studied the aggregation of different 1,1-disubstituted tetraphenylsiloles in poor solvents and observed the intriguing phenomenon of a dramatic increase in their light emission upon the formation of nanoclusters and aggregates, that is, aggregation-induced emission (AIE). For example, upon addition of nonsolvents into the solutions of 1-methyl-1,2,3,4,5-pentaphenylsilole, the silole molecules started to form nanodimensional aggregates and to emit intense blue light. The aggregation boosted the quantum yields by two orders of magnitude, turning the silole molecule from a weak luminophor (with quantum yield in the order of $\sim 10^{-4}$) into a strong emitter. The electroluminescence (EL) devices constructed using the silole as emitting layer exhibited very high brightness ($\sim$10000 cd/m^2) and power efficiency ($\sim$20 lm/W) [13]. In this work, a series of new linear and cyclic polyenes including siloles (T2TPS), butadienes (TPBD), cyclcobutenes (HPDMCB), fulvenes (DPMF), and 4*H*-pyrans (MCholP; Scheme 1) are presented as novel organic luminescence molecules with aggregation-induced emission and the emission color of these polyenes ranges from blue to red arising from the different chromophoric structures.

RESULTS AND DISCUSSION

Figure 1 shows the photoluminescence (PL) spectra of the thiophene substituted silole **T2TPS**. Almost no PL signals have been recorded



SCHEME 1

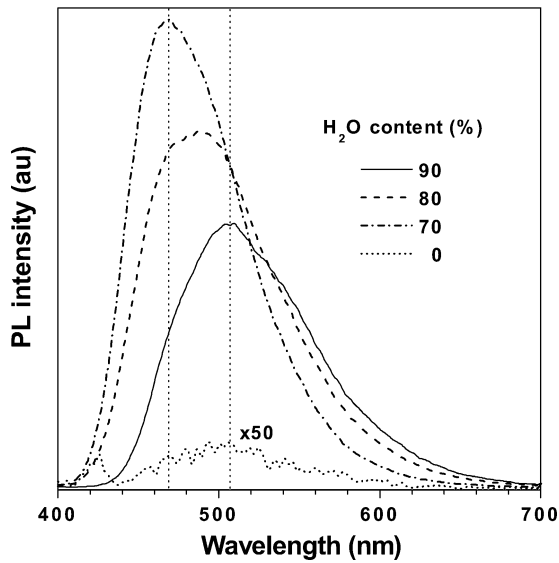


FIGURE 1 Photoluminescence spectra of **T2TPS** in acetone/water mixtures; [**T2TPS**] = 10 μM; excitation wavelength: 376 nm.

by a spectrofluorometer when a dilute acetone solution of **T2TPS** was excited at 376 nm. The molecule is thus a weak emitter when it is molecularly dissolved in a good solvent. Upon addition of large amounts of water to its acetone solutions (water/acetone ratio of 70:30 by volume, with the final concentrations of **T2TPS** being kept unchanged at 10 μM), intense blue light emission arises under identical measurement conditions ($\lambda_{max} = 470$ nm). Addition of water, as a nonsolvent of **T2TPS**, will lead to the formation of aggregates in the solvent mixtures. The resultant suspensions are macroscopically homogenous with no precipitate visible, suggesting that the silole aggregates are of nanodimension.

Somewhat to our surprise, the peak maximum of its fluorescence spectrum red-shifts from 470 nm to 505 nm when the water content further increases from 70% to 90%, which has not been observed for other silole congeners [9,10,13]. This phenomenon may be caused by the kinetics of their molecular packing arrangement. Solvent mixtures with water contents of less than 70% lead to a slow formation of the nanoaggregates, leaving sufficient time for the silole molecules to pack in a proper way (thermodynamically controlled). The packing is close to that of its single crystal, which is further supported by their pure blue emission color (PL of single crystals: $\lambda_{max} = 470$ nm [14]). If the water content is higher than 70%, the **T2TPS** molecules will cluster together too quickly and form random aggregates in an uncontrolled manner (kinetically controlled) with their emission peaking at 505 nm. This assumption is supported by the fact that the emission spectra of **T2TPS** in the 80% water content blue shifts after standing at room temperature for 12 h as shown in Figure 2.

Under the illumination of a 365-nm UV light at room temperature, **T2TPS** nanoparticles on the TLC plate show bright blue fluorescence.

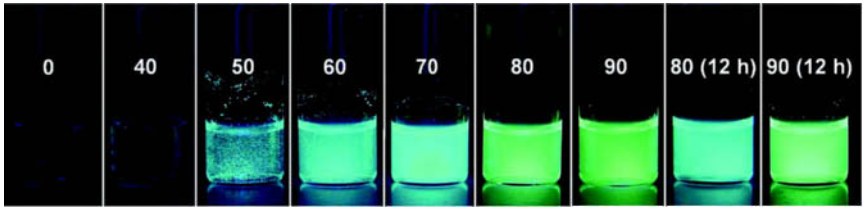


FIGURE 2 Photos of **T2TPS** taken under UV illumination in the water/acetone mixtures where water fractions (%) are labeled on the vials. [**T2TPS**] = 10 μM. The two samples on the right side are **T2TPS** in the 80% and 90% mixtures that stood at room temperature for 12 h.

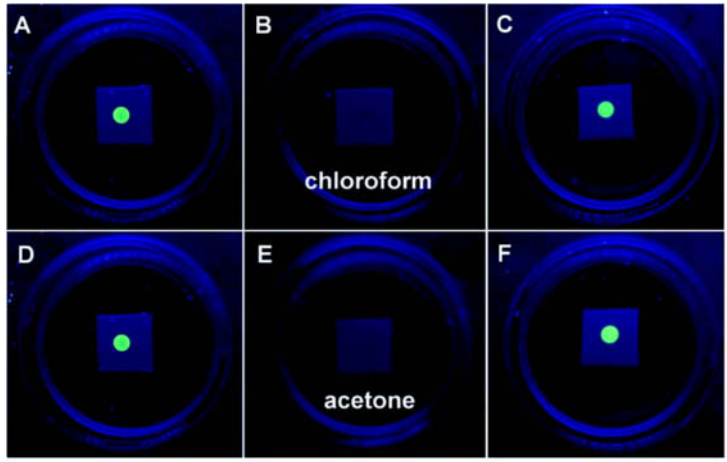


FIGURE 3 Photos of the **T2TPS** spots on the TLC plates in the Petri-dish sets in the (A and D) absence and (B and E) presence of vapors of organic solvents. Photos in C and F were taken after the solvents had been evaporated. All the photos were taken under UV illumination.

The intense light emission quenches upon exposure to solvent vapors and becomes visibly emissive again when the solvents are purged. This process is complete reversible and the fluorescence can be fully recovered after the solvents have been removed (Fig. 3). This

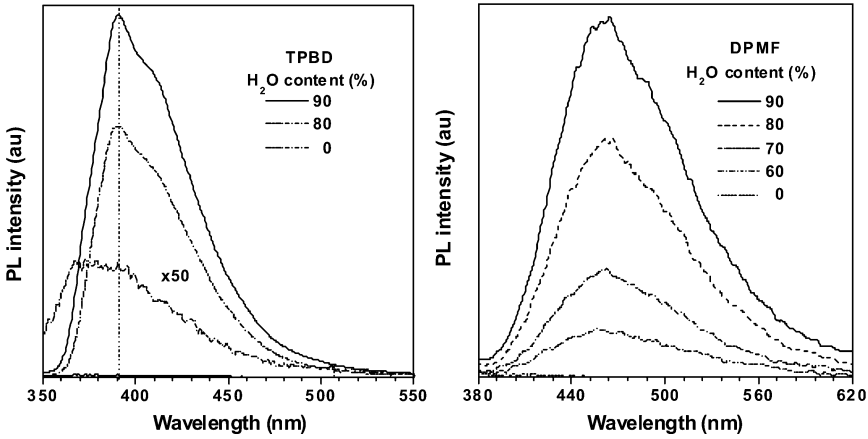


FIGURE 4 Photoluminescence spectra of **TPBD** and **DPMF** in acetonitrile/water mixtures; concentration: 10 μM; excitation wavelength: 330 nm.

fluorescence switching behavior makes the **T2TPS** nanoparticles a promising candidate for fluorescence devices sensing volatile organic compounds.

Upon addition of large amounts of poor solvent (water) into the solutions of **TPBD**, **DPMF** and **HPDMCB**, the light emissions of the dyes are boosted, similar to that observed in the **T2TPS** system. While the emission maximum of **TPBD** is at 390 nm, **DPMF** exhibits a steady luminescence increase with its maximum at 460 nm (Fig. 4). Unlike **T2TPS**, no shifts in their emission peaks are observed. The PL of **HPDMCB** in the acetone/water mixtures increases with an increase in the water content, with $\lambda_{max} = 470$ nm for solutions containing 50 and 70% water (Fig. 5). Further increase in the nonsolvent fraction leads again to a more than 30 nm red shift in the PL spectrum. The reason for this different emission behavior might be due to the different crystallization and packing ability of these compounds. While **TPBD** and **DPMF** are relatively small and therefore have no difficulties to pack in a thermodynamic favorable arrangement, **T2TPS** and **HPDMCB** are sterically bulky, leading to kinetically controlled aggregation of the dye molecules under the same experimental conditions.

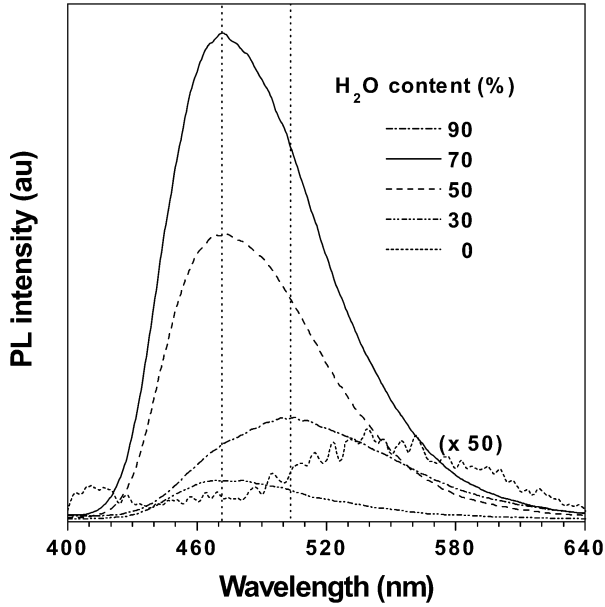


FIGURE 5 Photoluminescence spectra of **HPDMCB** in acetone/water mixtures; [**HPDMCB**] = 10 μM; excitation wavelength: 367 nm.

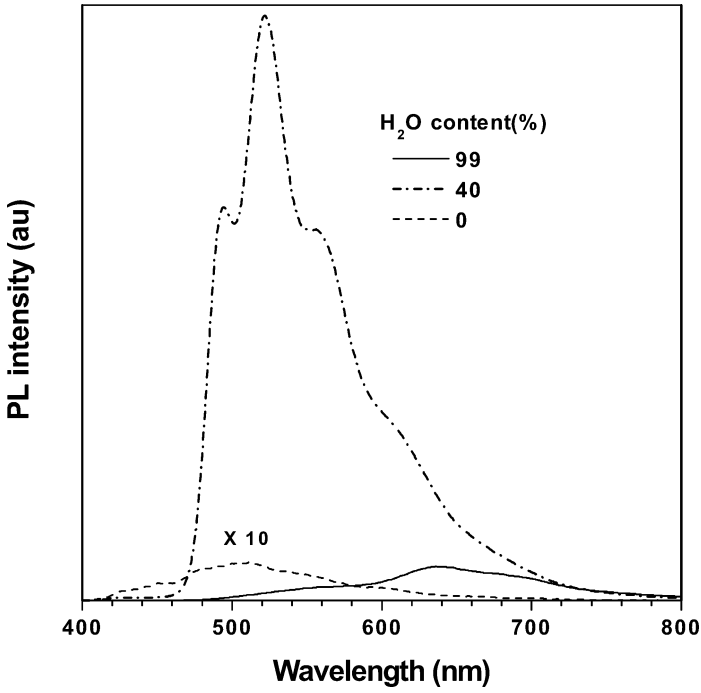


FIGURE 6 Photoluminescence spectra of **MCholP** in THF/water mixtures; [**MCholP**] = 10 μM; excitation wavelength: 370 nm.

Unlike previous compounds, **MCholP** contains a chiral cholesterol moiety, which may impart new chromophoric features such as polarized light emission. Figure 6 shows the PL spectra of a dilute THF solution of **MCholP**. The emission is very weak with its emission maximum centered at 508 nm. The addition of water boosts the fluorescence and an intense green emission of 523 nm can be observed at a water content of 40%. Further increase of the water content to 99% (while keeping its concentration constant) decreases the emission intensity but shifts its maximum dramatically for more than 100 nm to 640 nm, turning **MCholP** from a green to a red emitter. Similar to **T2TPS** and **HPDMCB**, the packing of the **MCholP** molecules will have influenced its fluorescence properties. When the water content is increased to ~40%, the majority of the **MCholP** molecules starts to aggregate into nanocrystals with intense green light emission. Since the THF content is high enough, the molecules can align properly and crystallize slowly (thermodynamically controlled). In contrast, at

a water content of as high as 99%, the particles will cluster very quickly, resulting in a random or kinetically controlled order.

Just as we have speculated, the emitted green light of **MCholP** is a polarized emission (with the polarization value $\sim$0.446). However, the red light of the solution with a water content of 99% is a normal isotropic emission. This becomes immediately clear if the previous findings are considered. The controlled packing of the **MCholP** molecules may lead to a formation of a helical structure, due to the combination of the pyranylidene malonitrile head group, with its large dipole moment, and the chiral cholesterol groups, which results in the polarized green emission. Meanwhile, the addition of large amounts of nonsolvent leads to an uncontrolled aggregation, which may not allow such a highly ordered secondary structure to form and will thus yield a normal isotropic emission.

CONCLUSION

In summary, a series of new linear and cyclic polyenes including siloles, butadienes, cyclcobutenes, fulvenes, and 4*H*-pyrans are reported as novel AIE materials. The emission color of these polyenes ranges from blue to red arising from the different chromophoric structures. The different aggregation states dramatically influence their emissions behaviors, including the emission intensity and maximum. Their emissions on the TLC plates can be quenched upon exposure to organic solvent vapors and become visibly emissive again when the solvents are removed. For 4*H*-pyrans bearing cholesterol moieties, green and red emissions can be observed at different solvent ratios. While the green light is a polarized emission, the red light is a normal isotropic emission.

REFERENCES

[1] Tang, C. W. & Vanslyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.
[2] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes A. B. (1990). *Nature*, *347*, 539.
[3] Ego, C., Grimsdale, A. C., Uckert, F., Yu, G., Srdanov G., & Mullen, K. (2002). *Adv. Mater.*, *14*, 809.
[4] Tao, Y. T., Chuen, C. H., Ko, C. W., & Peng, W. (2002). *Chem. Mater.*, *14*, 4256.
[5] Friend, R. H., Gymer, R. W., Holms, A. B., Burroughes, J. H., Marks, R. N., Taliani, C., Bradley, D. D. C., Dos Santos, D. A., Brédas, J. L., Lögdlund M., & Salaneck, W. R. (1999). *Nature*, *397*, 121.
[6] Lee, J.-I., Klaerner, G., & Miller, R. D. (1999). *Chem. Mater.*, *11*, 1083.
[7] Setayesh, S., Grimsdale, A. C., Weil, T., Enkelmann, V., Mulllen, K., Meghdadi, F., List, E. J. W., & Leising, G. (2001). *J. Am. Chem. Soc.*, *123*, 946.

[8] Marsitzky, D., Vestberg, R., Blainey, P., Tang, B. T., Hawker, C. J., & Carter, K. R. (2001). *J. Am. Chem. Soc.*, *123*, 6965.
[9] Luo, J., Xie, Z., Lam, J. W. Y., Cheng, L., Chen, H., Qiu, C., Kwok, H. S., Zhan, X., Liu, Y., Zhu, D., & Tang, B. Z. (2001). *Chem. Commun.*, 1740.
[10] Tang, B. Z., Zhan, X., Yu, G., Lee, P. P. S., Liu, Y., & Zhu, D. (2001). *J. Mater. Chem.*, *11*, 2874.
[11] An, B., Kwon, S., Jung, S., & Park, S. Y. (2002). *J. Am. Chem. Soc.*, *124*, 14410.
[12] Jayanty, S. & Radhakrishnan, T. P. (2004). *Chem. Eur. J.*, *10*, 791.
[13] Chen, H., Lam, J. W. Y., Luo, J., Ho, Y. L., Tang, B. Z., Zhu, D., Wong, M., & Kwok, H. S. (2002). *Appl. Phys. Lett.*, *81*, 774.
[14] Dong, Y. & Tang, B. Z. unpublished results.