JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Facile Access to Extremely Efficient Energy-Transfer Pairs via an Unexpected Reaction of Squaraines with Ketones

Shuaijun Yang, Jingsong You,* Jingbo Lan, and Ge Gao*

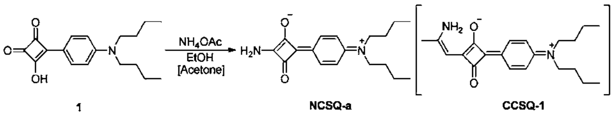
Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P.R. China

Supporting Information

ABSTRACT: We have discovered that squaraine **NCSQ** easily react with ketones in the presence of ammonium acetate to form a novel type of squaraine **CCSQ**. It is interesting to find that **NCSQ**s exhibit unusual solid-state fluorescence, whereas **CCSQ**s only exhibit fluorescence in solution. The quantum yield of solid **NCSQ-g** is measured to be 0.36, which is the highest among solid squaraines found so far. The large spectral overlap between the emission of **NCSQ**s and the absorption of **CCSQ**s, and the structural similarity of these molecules make them excellent energy-transfer (ET) pairs, as exemplified by the ET pair of **CCSQ-1**/**NCSQ-g**. When a very small amount (0.05 mol%) of **CCSQ-g** is doped into **NCSQ-g**, the ET efficiency reaches up to 96%. The Stern–Volmer quenching constant K_{SV} is calculated to be 65 800, indicating that **CCSQ-1**/**NCSQ-g** forms an extremely efficient ET pair. This study provides a novel skeleton and a facile route to efficient ET pairs.

Energy transfer (ET) from a host molecule (donor) to a guest molecule (acceptor) has attracted considerable attention because it can increase the solid-state emission of the guest, enlarge the Stokes shift to eliminate self-absorption, and tune emission color. Examples can be found in various systems such as organogels,[1] single crystals,[2] nanomaterials,[3] dendrimers,[4] and hybrid assemblies[5] for applications in photovoltaics and light-harvesting. In the 1960s through 1980s, ET in crystals was extensively studied, mainly focusing on the photophysical mechanism.[6] There are two prerequisites for a highly efficient ET system in the solid state: (1) a large spectral overlap of the emission and absorption of the host/guest and (2) a good structural similarity of the host/guest molecules. The most effective strategy to obtain such a system is to modify a good fluorescent skeleton to find two spectrum-matching molecules. In general, however, it is difficult to either synthesize or match these molecules. To date, [*n*]-acene derivatives[2b,6,7] and distyrylbenzene derivatives[8] are the most reported skeletons. Efficient ET pairs based on other skeletons are still rare,[9] which, to a certain extent, hinders the further development in this field. Herein we describe our serendipitous discovery of a squaraine skeleton **NCSQ** that exhibits unusual solid-state fluorescence with a record quantum yield among squaraines. More interestingly, **NCSQ** readily transforms to **CCSQ** under mild conditions, and the nearly perfect spectral match of **NCSQ**/**CCSQ** makes them efficient ET pairs in the solid state.

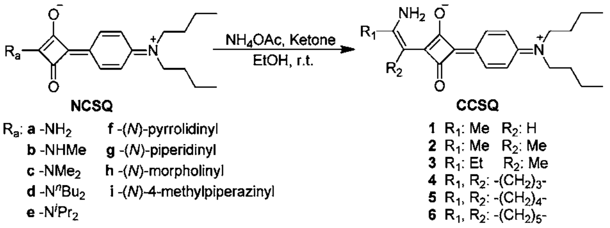
Squaraines are important functional fluorescent dyes and have extensive applications in solar cells, fluorescent probes, photodynamic therapy, and nonlinear optics.[10] Squaraines are usually characterized by large molar extinction coefficient, small Stokes shift, and strong solution fluorescence but no solid-state fluorescence. Because of our continuous interest in squaraines,[11] we reacted semi-squaraine **1** with ammonium acetate in ethanol to prepare unsymmetric squaraine **NCSQ-a** (eq 1).



(1)

When acetone was added into the reaction bottle during workup, to our surprise, the color of the reaction mixture rapidly turned from yellow to red. Thin-layer chromatography showed that the yellow spot that we originally considered to be the product vanished, and a new red spot appeared on the plate. These two spots were later isolated and characterized by ^{1}H NMR and X-ray diffraction (XRD) measurements. The yellow spot was proven to be the target unsymmetric squaraine **NCSQ-a** and the red spot to be a novel class of unsymmetric squaraine **CCSQ-1** (eq 1).

Further investigation showed that **NCSQ-a**–**NCSQ-i**, bearing different amino groups, could react with acetone in the presence of ammonium acetate in ethanol at room temperature to afford squaraine **CCSQ-1** (eq 2), and the results are summarized in Table S1. The primary, secondary, and tertiary amine derivatives reacted to give moderate yields (Table S1, entries a–c). There is a significant steric hindrance effect as demonstrated by a low yield of the reaction of the dibutylamine derivative **NCSQ-d**, and no reaction for the



(2)

Received: April 27, 2012
Published: June 29, 2012

dx.doi.org/10.1021/ja304082h | *J. Am. Chem. Soc.* 2012, 134, 11868–11871

diisopropylamine derivative **NCSQ-e**. Besides acetone, other ketones could also react with **NCSQs** to afford various **CCSQs**. Herein **NCSQ-g** was selected to react with different ketones as a typical example, and the results are summarized in Table S2. Substitution of acetone slowed the reaction rate (Table S2, entries 1−3). For butanone, the reaction preferred to take place at the 3-position rather than the 1-position. If a ketone has no α-carbon with at least two hydrogen atoms, no reaction occurs (Table S2, entry 7). Cyclopentanone and cyclohexanone reacted even faster than acetone but with lower yields (Table S2, entries 4 and 5). The mechanism was proposed to involve an enamine attacking the cyclobutene core of a protonated **NCSQ** to replace the amino group. (For the proposed reaction mechanism, see Supporting Information, IV.)

We also found that some **NCSQs** possessed strong fluorescence in the solid state, which is unusual because squaraines generally have no solid-state fluorescence due to strong non-covalent interactions between molecules.[10] For example, **NCSQ-g** exhibited green-colored fluorescence in THF and yellow-green-colored fluorescence (λ_{em} = 548 nm) with a quantum yield of 0.36 in the solid state (Figure 1b,d), to the best of our knowledge, which represents the highest fluorescence quantum efficiency in the solid state ever achieved among squaraines.[12] Other **NCSQs** showed similar fluorescence (Table S3). **NCSQ-a** and **NCSQ-b**, which respectively bear an amino and methylamino group on the cyclobutene core, showed no solid-state fluorescence, probably because both the amino and methylamino groups are so small that nonradiative decay of the excited state occurs through molecular relaxation.[13] Meanwhile, the product **CCSQs** contain an enamine moiety directly connected to the cyclobutene core. Thus, the lengthened conjugation made the fluorescence emission of the **CCSQs** red-shift. All the **CCSQs** have strong red fluorescence in solution (Table S4) but no solid-state fluorescence, suggesting that there exist strong intermolecular electronic interactions in the **CCSQ** solid. For example, the **CCSQ-1** solution in THF showed strong red fluorescence (λ_{em} = 605 nm, Φ = 0.62) (Figure 1c), but the crystals turned out to be dark-colored without any visible fluorescence.[14]

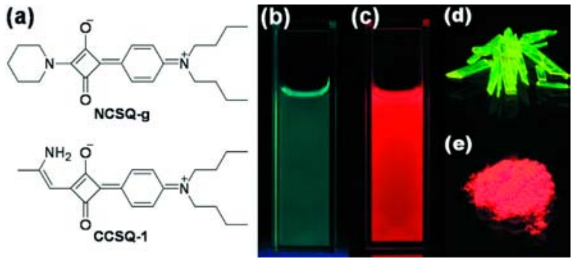


Figure 1. (a) Molecular structures of **NCSQ-g** and **CCSQ-1**. (b,c) Photos of **NCSQ-g** and **CCSQ-1** in THF (1.0×10^{-5} M) under UV light (λ_{ex} = 365 nm), respectively. (d) Photo of the crystals of **NCSQ-g** under UV light (λ_{ex} = 365 nm). (e) Photo of the **CCSQ-1**-doped **NCSQ-g** crystal powder (0.05 mol%) under UV light (λ_{ex} = 365 nm).

It was interesting to note that the emission of the solid **NCSQ-g** almost completely fell into the absorption band of **CCSQ-1** in solution (Figure 2a inset), and the spectral overlap integral $J(\lambda)$ was calculated to be 5.32×10^{15} M^{-1} cm^{-1} nm^{-4} (see Supporting Information, IX), which indicated a possible efficient ET from solid **NCSQ-g** to **CCSQ-1**. Subsequently, a variety of **NCSQ-g** solids doped with 0.0001−1.0 mol% of **CCSQ-1** were prepared by fast rotary evaporation of the solution of **NCSQ-g** and **CCSQ-1**. The fluorescence emissions of the doped powders were measured when excited at 365 nm, the maximum excitation of the solid **NCSQ-g** (Figures 2a and S2). With increasing amounts of **CCSQ-1**, the characteristic emission of **NCSQ-g** centered at 548 nm decreased gradually and shifted slightly to shorter wavelength; the emission of **CCSQ-1** emerged and increased gradually. This means that **NCSQ-g** absorbed light at 365 nm and transferred the energy to **CCSQ-1** to emit fluorescence. The emission of **CCSQ-1** reached its maximum at a **CCSQ-1**/**NCSQ-g** ratio of 0.01 mol % and subsequently started to quench when the **CCSQ-1**/**NCSQ-g** ratio kept increasing. Meanwhile, the emission of **CCSQ-1** moved gradually to longer wavelength. The plots of the fluorescent intensities of **NCSQ-g** and **CCSQ-1** and the ET efficiency versus the doping ratio are given in Figure 2b. They clearly show a very steep decrease of **NCSQ-1** accompanied with a rapid increase of **CCSQ-1** in the fluorescent intensities in a range of extremely low doping ratios. The ET efficiency (E_{ET}) already reached 96% at a doping ratio of 0.05 mol% (for the calculation, see Supporting Information, IX; for the photos under UV light and fluorescence microscope, see Figures 1e and S3, respectively), and there was an approximately 3-fold increase of the fluorescent intensity of the ET emission excited at 365 nm as compared with the emission of **CCSQ-1** excited at 560 nm (Figure 2c). By using the Stern−Volmer relation (see Supporting Information, IX), the Stern−Volmer quenching constant K_{SV} was calculated to be 65 800 (Figure S4), indicating that **CCSQ-1**/**NCSQ-g** formed an extremely efficient ET pair.[15]

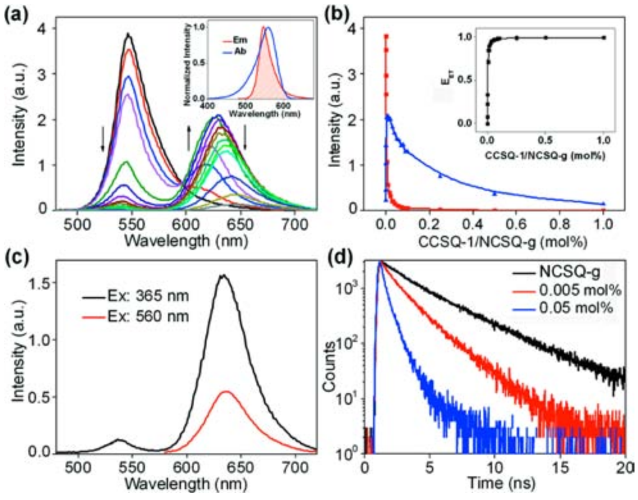


Figure 2. (a) Fluorescence spectra of **CCSQ-1**/**NCSQ-g** crystal powders at different ratios (0−1.0 mol%). Inset: Spectral overlap of the solid emission of **NCSQ-g** (red) and the absorption of **CCSQ-1** in THF (blue). (b) Emission maxima of **NCSQ-g** (red) and **CCSQ-1** (blue) plotted against the ratio of **CCSQ-1**/**NCSQ-g**. Inset: Plot of the energy-transfer efficiency (E_{ET}) versus the doping ratio. (c) Fluorescence spectra of the 0.05 mol%**CCSQ-1**-doped **NCSQ-g** crystal powder, excited at 365 (black) and 560 nm (red). (d) Lifetime decay profiles of the **CCSQ-1**/**NCSQ-g** crystal powders at different ratios.

At a doping ratio of 0.01 mol%, the ET efficiency was 85%, showing that as much as 8500 **NCSQ-g** molecules were quenched by a single **CCSQ-1** molecule.[7a] At this concentration, the distance between two neighboring **CCSQ-1** molecules could be estimated as 17 nm (see Supporting Information, IX). This long distance suggested that both FRET and exciton migration may be involved in this ET process.[16] Fluorescence lifetime decay profiles monitored at the emission of **NCSQ-g** showed that the fluorescence decay time decreased from 3.72 ns for pure **NCSQ-g** to 0.66 ns for the 0.05 mol% **CCSQ-1**-doped **NCSQ-g** (Figure 2d and Table S5), which further confirmed the efficient ET process. The ET rate (k_{ET}) was calculated to be 1.25×10^9 s^{-1} (see Supporting Information, IX), which was comparable with those of other solid-state ET systems.[2c] However, in solution, the ET process was not observed, and the solution of **CCSQ-1**/**NCSQ-g** only showed weak green-colored fluorescence under UV irradiation, characteristic of the emission of **NCSQ-g** in solution (Figure S5).

To gain insight into the solid-state emission behavior of this novel ET system, single crystals of **NCSQ-g** and **CCSQ-1** were grown by slow evaporation in CH_2Cl_2/CH_3OH, respectively. XRD measurements revealed that the structure of **NCSQ-g** is similar to that of **CCSQ-1** (Figures 3a,b and S7), but the stacking patterns are different (Table S6). The crystals of **NCSQ-g** are in the monoclinic space group $P2_1/n$. In the crystals, two **NCSQ-g** molecules are paired head-to-tail by the weak interactions of one oxygen atom of the cyclobutene core with one α-C−H of the dibutylamino group. Each pair is connected vertically by the weak interactions of the other oxygen on the cyclobutene core with one α-C−H of the piperidinyl group to form a zigzag structure (Figure 3c). All **NCSQ-g** molecules are staggered one by one, and no $\pi-\pi$ stacking could be observed (Figure S8), which accounts for its solid-state fluorescence.[17] Unlike **NCSQ-g**, **CCSQ-1** was determined in the triclinic space group $P\bar{1}$. In the crystals, one N−H of the enamine moiety forms a strong intramolecular hydrogen bond with one oxygen of the cyclobutene core (N−H···O, 1.832 Å), which rigidifies the **CCSQ-1** skeleton and may contribute to its strong fluorescence in THF (Φ = 0.62).[13] The other N−H, together with an α-C−H of the enamine group, form intermolecular hydrogen bonds with one oxygen of the cyclobutene core of the neighboring molecule (N−H···O, 1.887 Å; C−H···O, 2.711 Å), which connect the **CCSQ-1** molecules to construct a planar layer (Figure 3d). The signals of these two distinguishable N−H's of the enamine moiety are well separated in ^{1}H NMR spectra, which is characteristic of all **CCSQs**. The distance between these layers is as short as 3.118 Å, which is significantly short compared with the typical $\pi-\pi$ stackings (Figures 3e and S9).[18] The strong $\pi-\pi$ stackings between these layers cause fluorescence quenching of **CCSQ-1** in the solid state.[19]

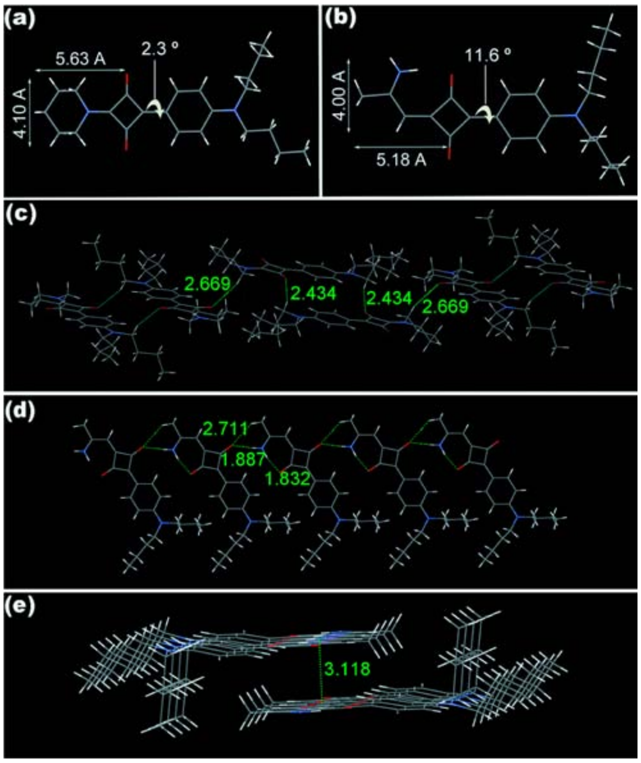


Figure 3. (a,b) Wireframe-style molecular structures of **NCSQ-g** and **CCSQ-1**, respectively. (c) Zigzag structure in the **NCSQ-g** crystals. (d) Intra- and intermolecular hydrogen bonds in the **CCSQ-1** crystals. (e) Planar layers in the **CCSQ-1** crystals.

Co-crystals of **CCSQ-1**/**NCSQ-g** suitable for X-ray analysis were also obtained from CH_2Cl_2/CH_3OH (Figure S10). However, the signals of **CCSQ-1** were not detected at all in the co-crystals, and the cell parameters were almost exactly the same as those of the pure **NCSQ-g** (Table S6). HPLC analysis of the co-crystals revealed a doping ratio of 4.7 mol% (Figure S11). These results suggested that the **CCSQ-1** molecules randomly replaced the **NCSQ-g** molecules in the latter crystal lattices, but did not break the latter lattices.[2b] Powder X-ray diffraction (PXRD) measurements also indicated that the **NCSQ-g** solids doped with different amounts of **CCSQ-1** showed XRD patterns identical to those of the pure **NCSQ-g** single crystals (Figure S12), which was in accordance with the X-ray analysis of the co-crystals.

CCSQ-1/**NCSQ-g** meets both of the aforementioned prerequisites and thus forms an extremely efficient ET pair. So we may easily tune the fluorescent emission color of the doped powders by varying the doping ratio. In the absence of **CCSQ-1**, **NCSQ-g** exhibits yellow-green fluorescence. Upon doping different amounts of **CCSQ-1** (0.001−0.5 mol%), the fluorescence color changes to yellow, orange, red, and scarlet (Figure 4). In addition, it should be pointed out that all **NCSQs** (**c**−**i**) could form efficient ET pairs with any one of **CCSQs** (**1**−**6**) (Table S7).

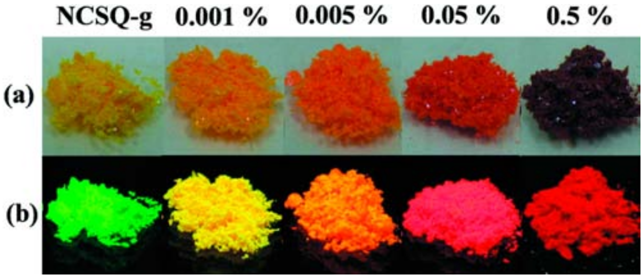


Figure 4. Photos of the **CCSQ-1**-doped **NCSQ-g** crystal powders (0, 0.001, 0.005, 0.05, and 0.5 mol%) under room light (top) and UV light (λ_{ex} = 365 nm, bottom).

In conclusion, we herein report a novel multicomponent reaction of **NCSQ** with ketone and ammonium acetate in ethanol to afford **CCSQ**. It is interesting that the reactant **NCSQs** show solid-state fluorescence with a quantum yield as high as 0.36, which is the highest among squaraines. Importantly, there exists efficient ET from **NCSQs** to **CCSQs** in the solid state, which has been demonstrated by the high ET efficiency at a quite low doping ratio of **CCSQ-1**/**NCSQ-g** (96% at 0.05 mol%). This high ET efficiency is attributed to the large overlap of the emission of **NCSQ-g** with the absorption of **CCSQ-1** and the high structural similarity of the two molecules. By doping very small amounts of **CCSQ-1** into **NCSQ-g** (0–0.5 mol%), a variety of fluorescence colors from yellow-green to scarlet can be obtained. This study provides a novel skeleton and an easy method for efficient ET pairs. This type of ET from reactants to products may be applied for designing highly sensitive solid fluorescent sensors. Further study of this reaction and the applications of this ET system are still underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, mechanism of the reaction, UV−vis, fluorescence, PXRD, fluorescence microscopy image, single crystal data, and equations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

jsyou@scu.edu.cn; gg2b@scu.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by grants from the National Natural Science Foundation of China (Nos. 21025205, 20972102, 21021001, 20902063, 21172159, and 21172155) and the National Basic Research Program of China (973 Program, 2011CB808600). We also thank the Centre of Testing and Analysis, Sichuan University, for XRD and NMR spectroscopic measurements.

■ REFERENCES

(1) Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C. *Chem. Soc. Rev.* **2008**, *37*, 109.

(2) (a) Nakanotani, H.; Saito, M.; Nakamura, H.; Adachi, C. *Adv. Funct. Mater.* **2010**, *20*, 1610. (b) Li, J.; Takaishi, S.; Fujinuma, N.; Endo, K.; Yamashita, M.; Matsuzaki, H.; Okamoto, H.; Sawabe, K.; Takenobu, T.; Iwasa, Y. *J. Mater. Chem.* **2011**, *21*, 17662. (c) Wang, H.; Li, F.; Gao, B.; Xie, Z.; Liu, S.; Wang, C.; Hu, D.; Shen, F.; Xu, Y.; Shang, H.; Chen, Q.; Ma, Y.; Sun, H. *Cryst. Growth Des.* **2009**, *9*, 4945.

(3) (a) For a review, see: Zhang, C.; Zhao, Y. S.; Yao, J. *New J. Chem.* **2011**, *35*, 973. (b) Wu, C.; Zheng, Y.; Szymanski, C.; McNeill, J. *J. Phys. Chem. C* **2008**, *112*, 1772. (c) Jin, Y.; Ye, F.; Zeigler, M.; Wu, C.; Chiu, D. T. *ACS Nano* **2011**, *5*, 1468.

(4) (a) Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489. (b) Hahn, U.; Gorka, M.; Vögtle, F.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 3595. (c) Balzani, V.; Ceroni, P.; Gestermann, S.; Gorka, M.; Kauffmann, C.; Vögtle, F. *Tetrahedron* **2002**, *58*, 629. (d) Zeng, Y.; Li, Y.; Li, M.; Yang, G.; Li, Y. *J. Am. Chem. Soc.* **2009**, *131*, 9100.

(5) For a review, see: Rao, K. V.; Datta, K. K. R.; Eswaramoorthy, M.; George, S. J. *Chem.—Eur. J.* **2012**, *18*, 2184.

(6) (a) Wolf, H. C. *Adv. At. Mol. Phys.* **1967**, *3*, 119. (b) Powell, R. C.; Soos, Z. G. *J. Lumin.* **1975**, *11*, 1.

(7) (a) Del Guerzo, A.; Olive, A. G. L.; Reichwagen, J.; Hopf, H.; Desvergne, J.-P. *J. Am. Chem. Soc.* **2005**, *127*, 17984. (b) Giansante, C.; Raffy, G.; Schäfer, C.; Rahma, H.; Kao, M. T.; Olive, A. G. L.; Del Guerzo, A. *J. Am. Chem. Soc.* **2011**, *133*, 316. (c) Olive, A. G. L.; Del Guerzo, A.; Schäfer, C.; Belin, C.; Raffy, G.; Giansante, C. *J. Phys. Chem. C* **2010**, *114*, 10410. (d) Zheng, J. Y.; Zhang, C.; Zhao, Y. S.; Yao. *J. Phys. Chem. Chem. Phys.* **2010**, *12*, 12935.

(8) (a) Ajayaghosh, A.; Vijayakumar, C.; Praveen, V. K.; Babu, S. S.; Varghese, R. *J. Am. Chem. Soc.* **2006**, *128*, 7174. (b) Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C.; George, S. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6260. (c) Hoeben, F.; Herz, L. M.; Daniel, C.; Jonkheijm, P.; Schenning, A.; Silva, C.; Meskers, S. C. J.; Beljonne, D.; Phillips, R. T.; Friend, R. H.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1976. (d) Hoeben, F. J. M.; Shklyarevskiy, I. O.; Pouderoijen, M. J.; Engelkamp, H.; Schenning, A.; Christianen, P. C. M.; Maan, J. C.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 1232.

(9) (a) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229. (b) Ishi-i, T.; Murakami, K.; Imai, Y.; Mataka, S. *J. Org. Chem.* **2006**, *71*, 5752. (c) Shu, T.; Wu, J.; Lu, M.; Chen, L.; Yi, T.; Li, F.; Huang, C. *J. Mater. Chem.* **2008**, *18*, 886. (d) Tseng, K.-P.; Fang, F.-C.; Shyue, J.-J.; Wong, K.-T.; Raffy, G.; Del Guerzo, A.; Bassani, D. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7032. (e) Ren, Y.; Kan, W. H.; Thangadurai, V.; Baumgartner, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 3964. (f) Papagni, A.; Del Buttero, P.; Moret, M.; Sassella, A.; Miozzo, L.; Ridolfi, G. *Chem. Mater.* **2003**, *15*, 5010.

(10) For reviews, see: (a) Ajayaghosh, A. *Acc. Chem. Res.* **2005**, *38*, 449. (b) Sreejith, S.; Carol, P.; Chithra, P.; Ajayaghosh, A. *J. Mater. Chem.* **2008**, *18*, 264. (c) Gassensmith, J. J.; Baumes, J. M.; Smith, B. D. *Chem. Commun.* **2009**, 6329. (d) McEwen, J. J.; Wallace, K. J. *Chem. Commun.* **2009**, 6339. (e) Beverina, L.; Salice, P. *Eur. J. Org. Chem.* **2010**, 1207. (f) Avirah, R. R.; Jayaram, D. T.; Adarsh, N.; Ramaiah, D. *Org. Biomol. Chem.* **2012**, *10*, 911.

(11) (a) Wang, W.; Fu, A.; You, J.; Gao, G.; Lan, J.; Chen, L. *Tetrahedron* **2010**, *66*, 3695. (b) Wang, W.; Fu, A.; Lan, J.; Gao, G.; You, J.; Chen, L. *Chem.—Eur. J.* **2010**, *16*, 5129.

(12) Matsui et al. just reported that an *N*-butyl indolenine squaraine derivative could emit solid-state fluorescence when enclathrated with toluene and *p*-xylene, but the quantum yield was only 0.02: Matsui, M.; Fukushima, M.; Kubota, Y.; Funabiki, K.; Shiro, M. *Tetrahedron* **2012**, *68*, 1931.

(13) Law, K.-Y. *Mol. Supramol. Photochem.* **1997**, *1*, 519.

(14) Actually, a very tiny emission peak at 738 nm was observed when solid **CCSQ-1** was excited at 680 nm (Figure S1).

(15) Wu, C.; Peng, H.; Jiang, Y.; McNeill, J. *J. Phys. Chem. B* **2006**, *110*, 14148. (b) Bhattacharyya, S.; Paramanik, B.; Patra, A. *J. Phys. Chem. C* **2011**, *115*, 20832.

(16) (a) Van Der Meer, B. W.; Coker, G.; Chen, S. Y. *Resonance Energy Transfer*; VCH: New York, 1994. (b) Huppert, D.; Rojansky, D. *Chem. Phys. Lett.* **1985**, *114*, 149.

(17) (a) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449. (b) Law, K.-Y. *Handbook Org. Cond. Mol. Polym.* **1997**, *1*, 487.

(18) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley & Sons: Chichester, U.K., 2009.

(19) For a review, see: Shimizu, M.; Hiyama, T. *Chem. Asian J.* **2010**, *5*, 1516.