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Isomer Restriction on a Nanoparticle Surface and Enhanced Blue Emission

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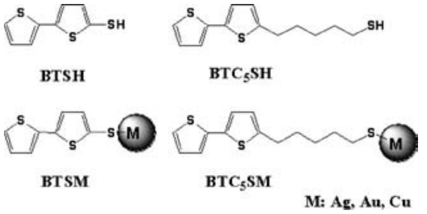
With the wide application of molecular fluorescence-based measurements and devices in chemistry, biology, medicine, and the material sciences, nanoparticle (NP) enhanced emission has attracted significant interest.[1−12] The emission enhancement is particle size and shape dependent,[1−11] and it is believed that electronic interaction between the ligand and metal core plays a key role. Coupling of a fluorophore with the plasmon resonance of the NPs enhances the emission,[11,13−15] as does structural restriction on an NP surface.[15] Recently, we reported the electron transfer and photopolymerization of 5-mercapto-2,2′-bithiophene (BTSH) functionalized Au NPs with different diameters (∼2, ∼4, and ∼6 nm)[16] and found that photopolymerization represents a facile method for making two- or three-dimensional designs of polythiophene nanomaterials. Interestingly, a size related blue emission with a peak around 455 nm from the nonpolymerized functionalized NPs, BTSMs (M: Cu, Ag, and Au), was observed, even though no emission of BTSH was detected with similar exposures. The emission goes away after photopolymerization (Figure 1 and Figures S1,S2). The UV absorption, emission, and excitation spectra of BTSAg NPs are shown in Figure 2a.

The electronic interaction among the ligands and NP core likely restricts the *cis* to *trans* isomerization of BTSH and the NPs causing the enhanced emission. To investigate this, 5-(5-mercaptopentyl)-2,2′-bithiophene (BTC_5SH) was synthesized (Supporting Information) and used as a control. The structures of BTSH, BTSM, BTC_5SH, and BTC_5SM are shown in Scheme 1.

Scheme 1. Structures of BTSH, BTSM, BTC_5SH, and BTC_5SM



The characteristics of the UV absorption of BTC_5SH can be identified from the absorption of BTC_5SM's (Figure 2b and Figure S3) by comparison with the spectra of BTSM's where an enhanced shoulder absorption around 390 nm is observed. Since BTSH has no emission at room temperature, the 455 nm emission of BTSM must be due to a new excited state. The average emission lifetime of BTSM is around 3 ns (Figure S4 and Table S1) so emission from BTSM in the charge separated state [$^{\bullet+}$BTSM(e)] is ruled out. Theoretical calculations at the B3LYP/6−31+G* level show that the energy of *cis*-BTSH in the ground state with a twist angle between two thiophene rings of 34° is ∼2.51 kJ mol^{-1} higher than that of *trans*-BTSH with a twist angle of 158°. The energy barrier between *cis*- and *trans*-BTSH is ∼9.62 kJ mol^{-1}. Based on Boltzmann distribution theory, 60% of *trans*-BTSH and 40% of *cis*-BTSH are estimated as present at 298 K, while 98% of *trans*-BTSH and 2% of *cis*-BTSH are estimated at 77 K. H^1 NMR spectra shift to the low field region with a decrease in temperature. Spectra at 298, 243, 223, and 203 K show chemical shifts that are clearly the result of the isomers of BTSH (Figure 3a and Figure S5). The peak distance between 3(H) and 3′(H) is increased from 0.020 to 0.040 ppm due to twisting of the thiophene rings.

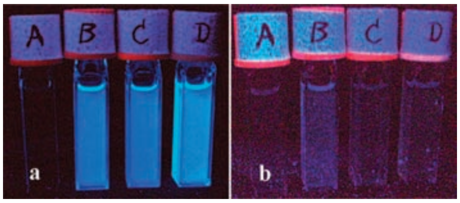


Figure 1. Photos taken under 366-nm UV lamp before (a) and after (b) irradiation (25 min with 350-nm UV light in toluene); A: BTSH; B: 2-nm BTSAg; C: 4-nm BTSAg; D: 6-nm BTSAg.

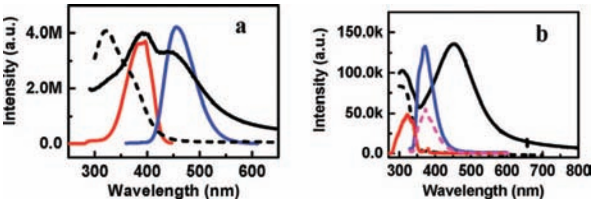


Figure 2. Emission spectra of 6-nm BTSAg (blue line) excited at 350 nm, UV absorption (black line) and excitation (red line) spectra of 6-nm BTSAg and the UV absorption of BTSH (black short dash line) (a). Emission spectra of 6-nm BTC_5SAg (blue line) excited at 320 nm. The UV absorption (black line) and excitation (red line) spectra of 6-nm BTC_5SAg, and UV absorption (black short dash line) and emission (magenta short dash line) spectra of BTC_5SH (b).

Strong emission from BTSH around 410 nm was observed in methylcyclohexane at 77 K, while no emission was observed at 298 K (Figure 3b and c). The fluorescence excitation spectrum detected at 410 nm shows a strong absorption around 326 nm and shoulder absorption in the short wavelength region (Figure 3c). This excitation spectrum is in accord with the calculations: 326 nm for the *trans*-isomer and 317 nm for the *cis*-isomer. This indicates that the *trans*-BTSH is emissive. Since the absorption spectrum of the *trans*-isomer is ∼10 nm red-shifted from that of the *cis*-isomer, the shoulder absorption around 390 nm recorded at room temperature must be attributed to the *trans*-isomer. The lower emission of BTSH at room temperature suggests that the thiol ligand loses energy rapidly through isomerization.

From the UV−visible spectral data, it is evident that the absorption around 390 nm of BTSM was enhanced relative to that of BTSH (Figure 2a and Figure S1) suggesting the *trans*-isomer is dominant on the surface of BTSM. The stability and structure of

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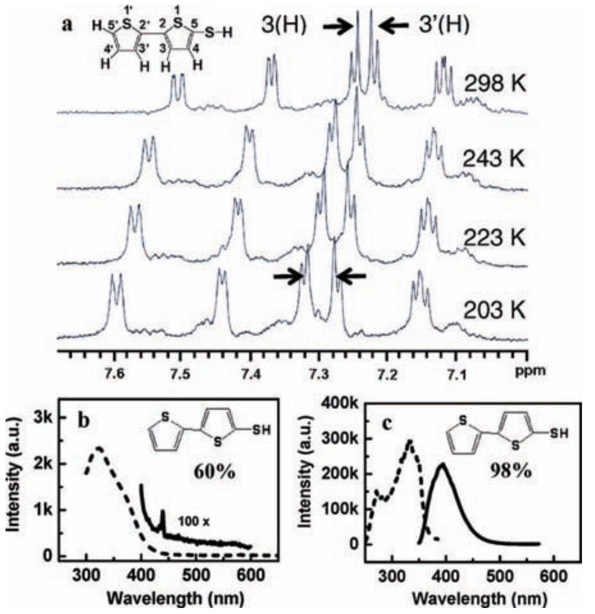
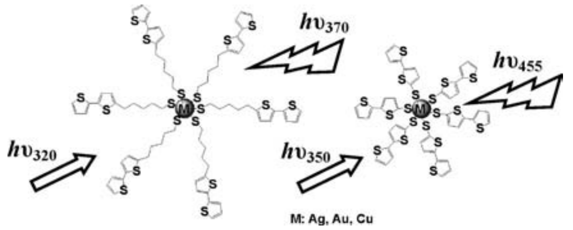


Figure 3. 400 Hz H^1 NMR spectra of BTSH in D-acetone at 298, 243, 223, and 203 K (a), absorption (short dash line) and emission (solid line) spectra of BTSH in methylcyclohexane at 298 K (b), and excitation (short dash line) and emission (solid line) spectra of BTSH in methylcyclohexane at 77 K (c).

the adsorbed molecule on the NP surface is dependent on interactions among neighboring molecules and the size of the particle.[17−19] Since molecules interact through intermolecular van der Waals forces to form well-packed monolayers on the NP surface,[20] and the *trans*-BTSH has lower energy than *cis*-BTSH, it is reasonable that the chemisorbed ligand maintains the *trans*-isomer structure restricting isomerization. Because *trans*-BTSH is emissive, the emission observed with BTSM probably relates to the *trans*-BTSH on the surface of the NP. The excitation spectrum in Figure 2a shows no signature of the Ag NP. The 455 nm emission mostly comes from the 390 nm absorption, not from the Ag nano core. In comparison, no new enhancement in absorption for BTC_5SM was observed in Figure 2b and Figure S3. Given the flexible methylene groups between the thiophene ring and the nano metal core in BTC_5SM, isomerization of the BT ring cannot be restricted by the nano metal core. Excitation spectra indicate the 370-nm emission of BTC_5SM comes from the ligand with an enhanced intensity (Figure 2b and Figure S3). Since the BT ring is ∼1 nm from the NP surface, ligand emission enhancement is reasonable due to the plasmon resonance of the Ag NP according to the former reports.[11,13−15] In contrast, in the case of BTSM, the BT ring is attached on the surface of the NP and the ligand emission is usually quenched due to energy or electron transfer. Therefore, the 455 nm emission of BTSM comes from the *trans*-BTSH on the surface of the NPs which forms an emissive excited state (Scheme 2). After photopolymerization, the linker between two NPs should be α-quaterthiophene formed by dimerization of two BTs and the blue emission fades away. Control experiments with the ligand 1-dodecanethiol ($C_{12}H_{25}SH$) were also carried out under similar conditions. No emission was detected (Figure S6).

In summary, *trans*-BTSH is of lower energy than the *cis*-isomer, the absorption of *trans*-BTSH is enhanced in BTSM, and the excitation spectrum of BTSM is the same as the absorption spectrum of *trans*-BTSH. Therefore we suggest that the *trans* isomer assembles on the NP surface giving the enhanced blue emission. No enhancement of ligand absorption and emission appears at different wavelengths indicating the isomer restriction does not occur in BTC_5SM with a flexible methylene chain in which the BT ring is 1 nm from the NP surface.

Scheme 2. Schematic of Ligands on the Surfaces of BTC_5SM and BTSM, respectively



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Supporting Information Available: UV absorption and emission spectra of BTSMs, BTC_5SMs, and photos taken under the long wavelength UV lamp before and after irradiation. Synthesis of BTC_5SH; Quantum yield and average lifetime of BTSMs; H^1 NMR spectra of BTSH at 298, 243, 223, and 203 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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