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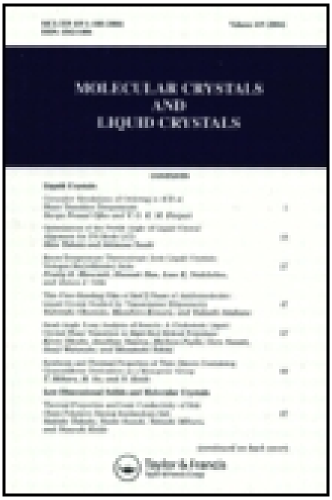

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Fluorescence Study on Organic Nanoparticles Prepared with ABCV-Th

Dong Myung Shin [a]
[a] Department of Chemical Engineering , Hongik University , Seoul, Korea

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Fluorescence Study on Organic Nanoparticles Prepared with ABCV-Th

Dong Myung Shin
Department of Chemical Engineering, Hongik University, Seoul, Korea

We have synthesized a new red fluorescent material (2E, 2′E)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th). Nonplanar structure of ABCV-Th resists on the concentration quenching, which is induced from dipole-dipole interactions and effective π-stacking in condensed states. Accordingly, ABCV-Th well exhibited photoluminescence in solid state. Intramolecular charge transfer (ICT) excited states of ABCV-Th were sensitive to the solvent polarity, and that exhibited bathochromic shift in polar solvents. Nanoparticles were prepared by using the reprecipitation method. The FE-SEM image reveals the size and physical characteristic of the nanoparticles.

Keywords: ABCV-Th; intramolecular chare transfer; nanoparticle; red-emissive

1. INTRODUCTION

The unique physical phenomena draw a lot of interest in the fluorescent inorganic semiconductor and metal nanoparticles. Quantum confinement effects and finite size of particles change optical and electrical properties of materials [1–2]. Optical spectrum of inorganic nanoparticles exhibits hypsochromic shift, compared to the bulk. Recently, fluorescent organic nanoparticles (FONs) have been studied due to their flexibility in synthesis and preparation. Nakanishi and co-workers have demonstrated that the fluorescent properties of FONs are dramatically dependent on the size and the physical statues of the materials [3–6].

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Address correspondence to Prof. Dong-Myung Shin, Department of Chemical Engineering, Hongik University, Sangsu-Dong, Mapo-Gu, Seoul, 121-791, Korea. E-mail: shindm@wow.hongik.ac.kr

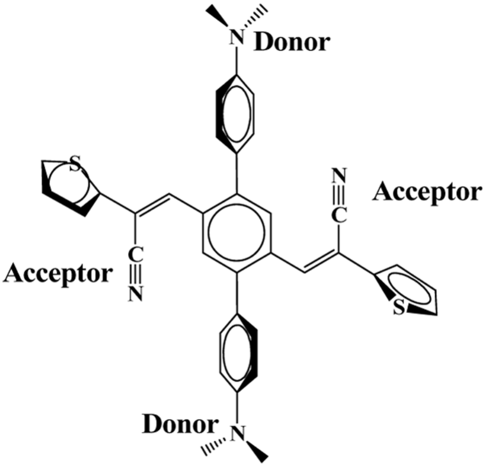


FIGURE 1 The molecular structure of ABCV-Th.

An intramolecular charge transfer(ICT) compound has electron-donating group(s) (D) and electron-accepting group(s) (A) which are connected through π-conjugated linker [12]. Solvatochromic effects and spectral changes under various physical and biological environments make the ICT compounds polarity tag [7–8].

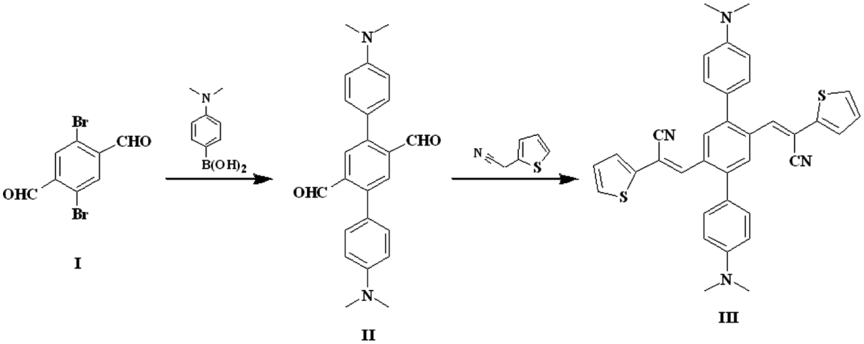
In the present work, a red light-emitting compound has been designed and synthesized. Figure 1 shows the characteristic molecular structure of new red fluorophore, (2*E*,2′*E*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th). This molecule has two electron donor-acceptor (D-A) moieties at central benzene ring and the π-electron resonance pathways between the donor and acceptor groups. Most of the red fluorescent organic materials do not emit in the solid state, but ABCV-Th can emit in the solid state. It also has ICT characteristics.

2. EXPERIMENTAL SECTION

2.1. Synthesis

(2E,2′E)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th) (Scheme 1)

(i) 2,5-dibromoterephthalaldehyde was obtained by oxidation of 1,4-dibromo-2,5-dimethylbenzene; (ii) 4,4″-bis(dimethylamino)-1,1′: 4′,1″- terphenyl-2′,5′-dicarbaldehyde was obtained catalytic cross Suzuki coupling reaction of 1,4-dibromo-2,5-dimethylbenzene with



SCHEME 1 Synthesis of (2*E*,2′*E*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th).

4-(dimethylamino)phenylboronic acid; (iii) (2*E*,2′*E*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th) was obtained Knoevenagel reaction of 4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-dicarbaldehyde with 2-thiophenacetonitrile. Yield: 61%; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.172 (s, 2H), 7.476 (s, 2H), 7.402 ~ 7.381 (m, 6H), 7.286 (d, 2H), 7.088 ~ 7.070 (dd, 2H), 6.833(d, 4H), 3.033(s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 40.598, 76.943, 77.200, 77.452, 107.368, 112.408, 117.342, 126.606, 126.660, 127.165, 128.257, 130.165, 131.292, 132.783, 139.532, 140.110, 140.819, 150.365; MS (FAB) calcd for $C_{36}H_{30}N_4S_2$ (M^+) m/z 582.19, found 582. The purity of ABCV-Th was confirmed by sharp melting point at 321°C.

2.2. Preparation of Nanoparticles

Nanoparticles were prepared by the reprecipitation method [9–11]. The ABCV-Th/THF solution ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) were injected 10 mL of distilled water with vigorous stirring at room temperature.

2.3. Measurement

Melting point of ABCV-Th was measured by differential scanning calorimetry (DSC) using a Mettler-Toredo DSC823. UV-visible absorption and photoluminescence (PL) were measured on a HP model 8453 and Perkin Elmer LS-50B, respectively. Field emission scanning electron microscopy (FE-SEM) images were observed on a JEOL model JSM-6700F. Variety images were acquired by Nikon-Coolpix P4 digital camera.

3. RESULTS AND DISCUSSIONS

This type of red fluorophore is vulnerable to concentration quenching in solid state owing to dipole-dipole interactions among the molecules. The ABCV-Th has two twisted intramolecular charge transfer (TICT) characters using two equivalent pairs of electron donors-acceptors, Figure 1. Many organic materials which have ICT characters do not emit at solid state due to dipole quenching. However, the ABCV-Th does not show concentration quenching because dipole-dipole interactions among the molecules are almost suppressed by the two equivalent antiparallel ICT dipoles. Figure 2 showed the normalized UV-visible absorption and photoluminescence (PL) spectra of ABCV-Th in chloroform and thin solid film deposited on quartz plate with a thickness of about 100 nm. The PL spectrum of solid film represented that ABCV-Th did not exhibit fluorescence quenching in solid state which was the usual property of red emitting materials. The PL spectra obtained from chloroform shows a peak at 597.5 nm, which shifted to 616 nm at solid state with excitation at 336 nm and 340 nm, respectively. The large Stokes shifts are due to considerable bathochromic shifts in emission, which are attributed to the presence of photo induced TICT excited states in the ABCV-Th molecule.

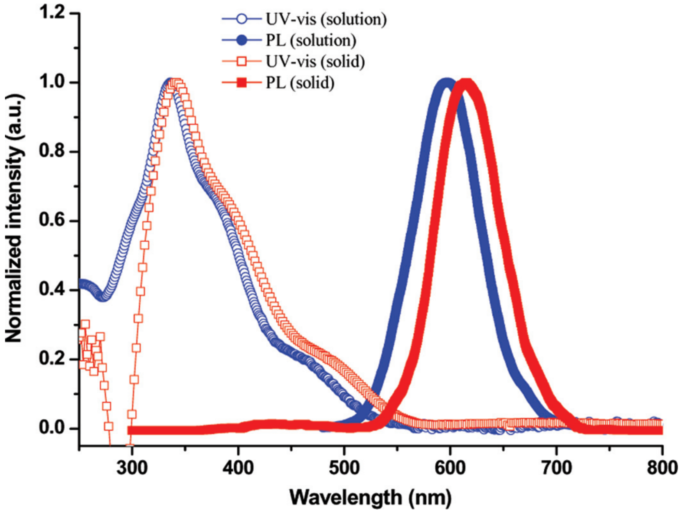
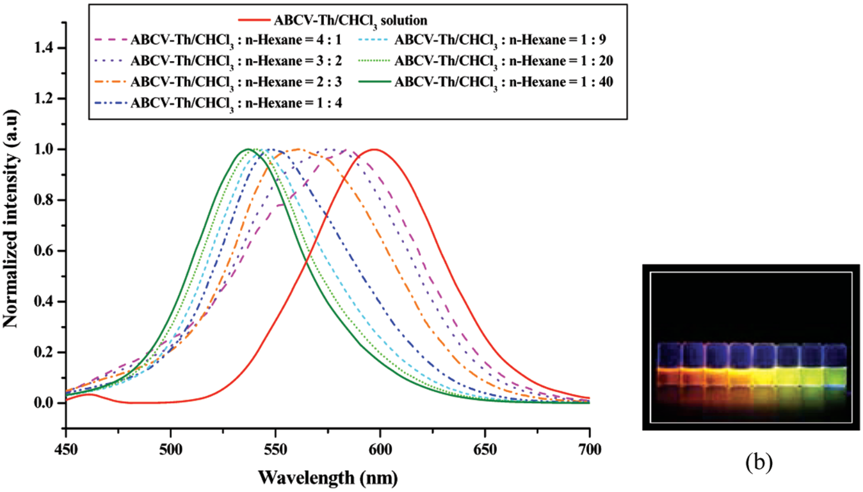


FIGURE 2 Normalized UV-vis absorption and photoluminescence spectra of ABCV-Th in chloroform and thin solid film deposited on quartz plate with a thickness of 100 nm.



(a) (b)

FIGURE 3 (a) Normalized PL spectra of ABCV-Th in various ratio solvents. (b) The fluorescence emission of ABCV-Th (1.0×10^{-4} mol L^{-1}) in CHCl$_3$ and n-Hexane mixture under the UV light (365 nm). The ratio of CHCl$_3$:n-Hexane from right to left are 1:0, 4:1, 3:2, 2:3, 1:4, 1:9, 1:20, 1:40.

Figure 3 shows PL spectra and emission of ABCV-Th under the UV light with changing solvent polarity. As the concentration of chloroform increases, the emission peak shifted from 537 to 597 nm. The fluorescence emission spectrum suffers a strong bathochromic shift,

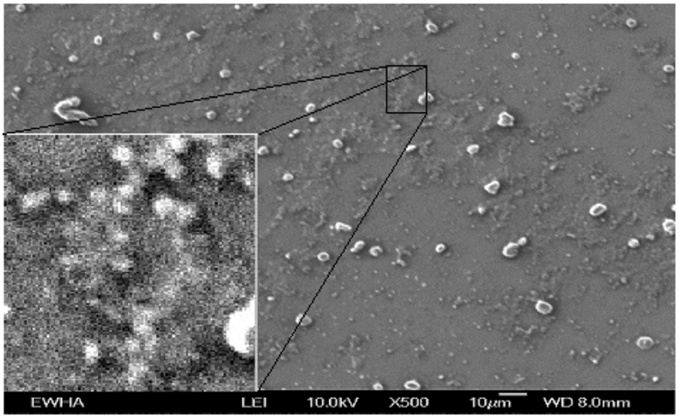
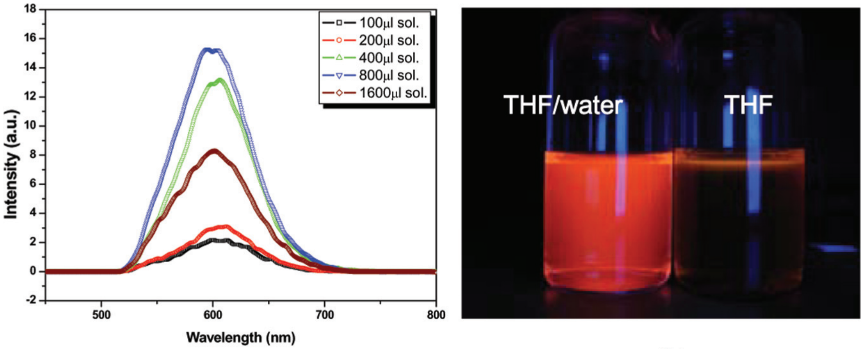


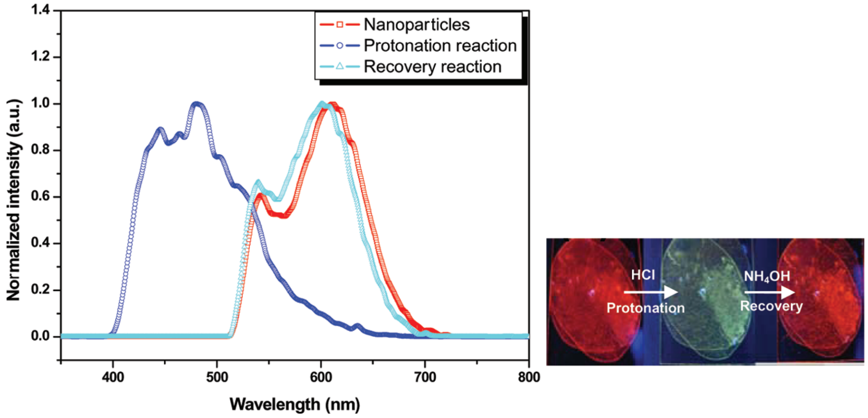
FIGURE 4 The SEM image of ABCV-Th nanoparticles.



(a) (b)

FIGURE 5 (a) Variation of PL spectra of ABCV-Th nanoparticle-suspension (THF/water) with the concentration of ABCV-Th, in which the injected ABCV-Th solution (1.0×10^{-4} M in THF) were 100 μl, 200 μl, 400 μl, 800 μl and 1600 μl. (b) The fluorescence emission of ABCV-Th nanoparticles suspension in THF/water and THF with irradiation of UV-light (365 nm).

60 nm, as the solvent polarity increase. The bathochromic shift indicates the π-π^* transition in the excited state. The shape of ABCV-Th nanoparticles was observed by The FE-SEM, Figure 4. The size variation was very large due to aggregation during preparation for SEM. Figure 5 showed variation of PL spectra of ABCV-Th



(a) (b)

FIGURE 6 The PL spectra of ABCV-Th nanoparticles. The changes in PL spectra after protonation reaction and the recovery reaction with base.

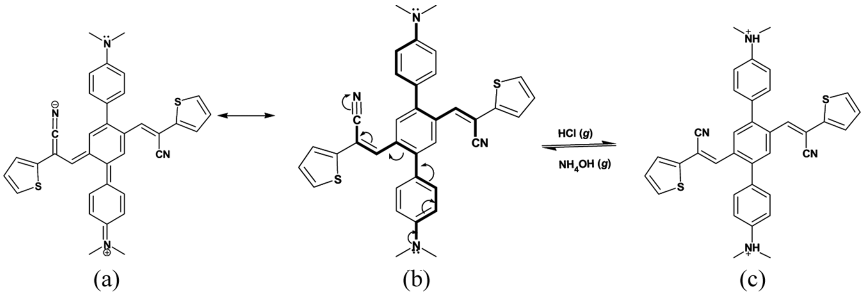


FIGURE 7 Mechanism on a protonation reaction and a recovery reaction. (a) ICT effect, (b) electron-donor and electron-acceptor (c) protonation reaction.

nanoparticles in THF/water with the concentration of ABCV-Th. As quantity of injected THF solution into water was increased, nanoparticle sizes were increased [9]. Until 800 µl of THF solution was injected into the water, emission intensity was noticeably increased due to formation of ABCV-Th nanoparticles. However, when 1600 µl THF solution was injected, intensity was substantially decreased because precipitation.

Figure 6 shows PL spectra of ABCV-Th nanoparticles and after those protonation and recovery reaction with ammonia. After protonation reaction, the maximum peak shifted to blue about 133 nm (611 nm to 480 nm). With protonation, the molecules lose electron donating ability, Figure 7.

4. CONCLUSIONS

A new red fluorescence material (2*E*,2′*E*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-thienyl)acrylonitrile] (ABCV-Th) has been synthesized and prepared as nanoparticles. The fluorescence spectra were changed by polarity of solvent, protonation and recovery reaction. ABCV-Th emits strongly at solid state with formation of nanoparticles.

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