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Substituent Effect on Color Tuning of Red Light Emission in Photoluminescence and Electroluminescence of Red Fluorophore

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Typical small red light-emitting molecules for organic light emitting diodes (OLEDs) were highly susceptible to fluorescence concentration quenching in solid state. Red fluorophores, (2Z, 2′Z)-3, 3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis(2-phenylacrylonitrile) (ABCV-P), (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) and (2*Z*, 2′*Z*)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis[2-(2-naphthyl)acrylonitrile] (ABCV-Np), capable of preventing fluorescence concentration quenching were designed and synthesized. These compounds have intramolecular charge transfer (ICT) properties which were estimated by measurement of UV-Visible absorption and photoluminescence (PL) emission spectra with variation of solvent polarity (*n*-Hexane/Chloroform = 99/1, 1/1; Chloroform; Methylene chloride). The magnitude of ICT for ABCV-Th was measured to be the largest and that for ABCV-Np was slightly larger compared to that for ABCV-P. The magnitude of ICT resulted in a shift of peak wavelength of PL emission. Therefore, this result well supported substituent effect on the color change of PL emission. The peak wavelengths of photoluminescence for ABCV-P, ABCV-Np and ABCV-Th were observed to be 607.5, 611.5 and 617.5 nm, respectively, and those of EL spectra were measured to be 612.5, 619.5, 621.0 nm, respectively. The emission maxima of PL and EL spectra for these red fluorescent compounds were well correlated with substituent effect on ICT for them.

Keywords: ABCV-P, ABCV-Np, ABCV-Th, Intramolecular Charge Transfer (ICT), The Color Change, Concentration Quenching, Stokes Shift.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted major attentions in recent years and are now being considered as the next-generation flat-panel displays due to their advantages, such as low operating voltage, low power consumption, self-emission, high contrast, fast response time, wide-viewing angle, ultrathin structure and light weight.[1–3] Light-emitting materials are one of the primary substances for OLEDs. Numerous fluorescent materials, including both the host-emitters and the dopants, have been known and developed since reports from Kodak on green OLEDs in 1987 and the green and red doped OLEDs in 1989.[4–5] A number of green and blue emissive materials used in OLEDs with high device performance have been reported.[6–9] However, the red fluorescent molecular materials have remained to be the weakest part in realizing the full color display with low efficiency and poor color purity.[3,10] Concentration quenching due to the interaction among the molecules at high concentration is common and serious problem for small molecule-based OLEDs. Most red light-emitting materials including pyran-containing donor–acceptor family, such as 4-(dicyanomethylene)-2-methyl-6-[*p*-(*N*,*N*-dimethylamino)-styryl]-4*H*-pyran (DCM1), 4-(dicyanomethylene)-2-methyl-6- (julolidine-4-yl-vinyl)-4*H*-pyran (DCM2) and 4-(dicyanomethylene)-2-*tert*-butyl-6-(1, 1, 7, 7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB), are highly prone to fluorescence concentration quenching due to aggregation in solid state.[3,10–12] A universal method for solving the concentration quenching problem of red emissive materials in OLED application

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is the use of them as a dopant in the host-guest doped emitter system. In doped red OLEDs, the control of the dopant concentration is very critical because inefficient energy transfer from the host will result in a mixture of two emission profiles and contribute to an unsaturated red emission.[12] Furthermore, the optimum dopant concentration is usually low, commonly no greater than 2%, and the effective doping range is extremely narrow and commonly no greater than ±0.5% of the optimum concentration.[10] Therefore, preventing of concentration quenching became important issue in development of red fluorescent materials.

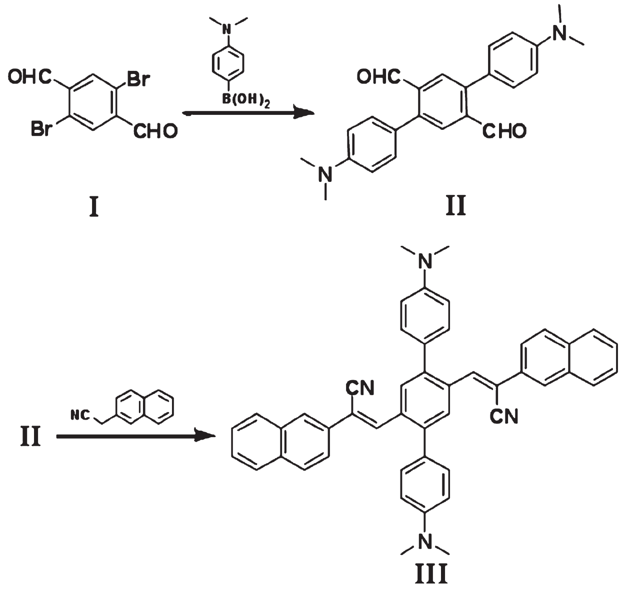
In this work, a new red fluorophore, (2*Z*, 2′*Z*)-3,3′-[4, 4″-bis(dimethylamino)-1, 1′:4′, 1″-terphenyl-2′, 5′-diyl]bis [2-(2-naph-thyl)acrylonitrile] (ABCV-Np), was synthesized in order to study on color tuning of emission from that molecular system which was controlled by variation of substituent in the molecule. For the purpose of quantitative analysis of degrees of color change in light emission by substituent effect, UV-visible absorption and photoluminescence (PL) spectra of fluorophores having various substituents with variation of solvent polarity were measured.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

Scheme 1 showed the synthetic procedure of red-emissive material, ABCV-Np.

All solvents involved in the experiments were reagent grade and were purified by the usual methods before use. The molecular structure of ABCV-Np was confirmed by the ^{1}H and ^{13}C-NMR spectra of its precursors and by H^1 and MS (FAB) spectra of ABCV-Np.



Scheme 1. The synthesis of ABCV-Np

2,5-Dibromoterephthalaldehyde (I) was prepared by the method of Evers and Moore.[13]

4,4″-Bis(dimethylamino)- 1,1′:4′,1″- terphenyl- 2′,5′-dicarbal-dehyde (II) was obtained from the reaction of 2,5-dibromote-rephthalaldehyde (I) with 4-(dimethylamino)phenylboronic acid by Suzuki coupling. The mixture of 2,5-dibromoterephthalaldehyde (I) (500 mg, 1.71 mmol), 4-(dimethylamino)phenylboronic acid (622 mg, 3.77 mmol), $Pd(PPh_3)_4$ (79 mg), Na_2CO_3 (540 mg) and Aliquat 336 (0.3 ml) in mixed solvent of toluene (40 ml)-H_2O (25 ml)-THF (10 ml) was mildly refluxed under N_2 atmosphere with stirring for 3 hr. The reaction mixture was cooled, filtered and washed with water and *n*-hexane. Removal of the solvents and drying under high vacuum afforded 600 mg (1.61 mmole) of the product (II) as a light yellow to orange solid and further purification was not required. Yield: 94%.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 10.105 (s, 2H), 8.060 (s, 2H), 7.315 (d, 4H), 6.830 (d, 4H), 3.048 (s, 12H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 192.85, 192.80, 150.45, 143.64, 136.36, 131.07, 129.88, 123.00, 112.15, 40.33.

(2*Z*, 2′*Z*)-3, 3′-[4, 4″-bis(dimethylamino)-1, 1′:4′, 1″-terphenyl-2′, 5′-diyl] bis [2-(2-naphthyl) acrylonitrile] (ABCV-Np) was prepared from the Knoevenagel reaction of 4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-dicarbaldehyde (II) with 2-naphthylacetonitrile. The mixture of 4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-dicarbaldehyde (II) (1.40 g, 3.76 mmol), 2-naphthylacetonitrile (1.51 g, 9.03 mmol) and sodium ethoxide (prepared by reaction of 207 mg of Na with 20 ml of absolute EtOH) in 340 ml of EtOH was stirred at room temperature for 4 days. The red solid formed in the reaction mixture was filtered and washed with water, EtOH and *n*-Hexane. The filtrate was further purified by recrystallization in $CHCl_3$/Acetone. Removal of the solvents and drying under high vacuum afforded 1.98 g (2.95 mmole) of the product (III) as a red solid. Melting point: 305.5 °C Yield: 78.5%; ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.281 (s, 2H), 8.188 (s, 2H), 7.913 (m, 2H), 7.853 (m, 4H), 7.807 (s, 2H), 7.683 (dd, 2H), 7.533 (m, 4H), 7.462 (d, 4H), 6.840 (d, 4H), 3.029 (s, 12H); MS (FAB) calcd. for $C_{48}H_{38}N_4$ (M^+) m/z 670, found 670.

2.2. Measurement

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.761 MHz and 125.701 MHz, respectively. A mass spectrum (FAB-MS) was measured on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) using standard conditions. The melting point was measured to be 305.5 °C by differential scanning calorimetry (DSC) using a TA Instruments, USA (Q-1000) with a scan rate of 5°C/min over the temperature range of

0 °C~350 °C. UV-visible absorption and PL emission spectra were measured by HP model 8453 and Perkin Elmer LS-55, respectively.

2.3. Fabrication of OLED and EL Measurement

The devices with the structure of ITO (100 nm)/NPB (40 nm)/red emitter (30 nm)/BCP (10 nm)/Alq3 (20 nm)/Liq (2 nm)/Al (100 nm) was fabricated by the high-vacuum thermal deposition (8×10^{-7} Torr) of organic materials onto the surface of indium tin oxide (ITO)-coated glass substrate. The deposition rates were 1.0~1.1 Å/sec for organic materials, 0.1 Å/sec for lithium quinolate (Liq) and 10 Å/sec for aluminum (Al) cathode. The EL emission spectra were recorded on Perkin Elmer LS-55 and device performance was measured using Keithley 236 and CHROMA METER CS-100A instruments.

3. RESULTS AND DISCUSSION

The conjugation system, the strength of electron donor and electron acceptor, the rigidity of the molecule and the steric hindrance has to be considered in the design of an intramolecular charge-transfer (ICT) fluorescent molecule. The molecular structures of the newly synthesized ABCV-Np and the widely reported red dopants, DCM2 and DCJTB,[14–18] were shown in Figure 1. The typical red dopants, DCM2 and DCJTB, with both strong electron donor and electron acceptor groups posses a high fluorescence quantum yield[10] and have ICT character. DCM-type red light-emitters, such as DCM2 and DCJTB, suffer from severe fluorescence concentration quenching in solid state due to both large dipole moments caused by pyran-containing donor–acceptor structures and their molecular planarities. These quenching phenomena limited the optimum dopant concentration and the effective doping range to a low doping concentration and narrow doping concentration range.[10, 19]

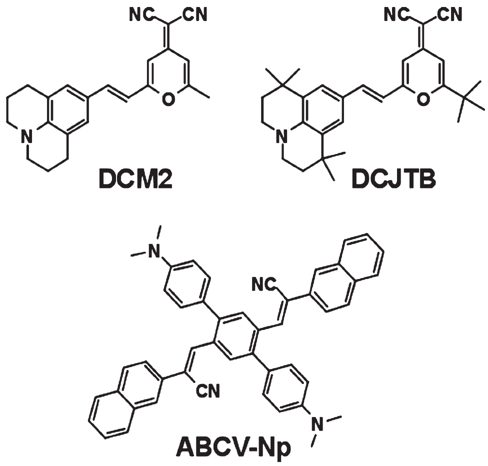


Fig. 1. The molecular structures of DCM2, DCJTB and ABCV-Np.

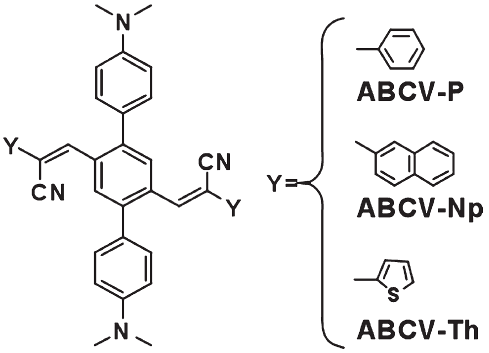


Fig. 2. The Variation of substituent at the carbon atom attached electron-withdrawing cyano group.

Therefore, preventing the fluorescence quenching is crucial for enhancing the dopant concentration and doping concentration range. ABCV-Np was designed to prevent this concentration quenching. As shown in Figure 1, The ABCV-Np molecule is almost nonpolar due to the cross arrangements of antiparallel, electron donor–donor and acceptor-acceptor pairs in the molecule. Furthermore, the molecular structure of ABCV-Np is highly noncoplanar due to its distorted molecular geometry caused by its twisted terphenyl backbone and the steric crowding on its central benzene ring being a part of that terphenyl.

Figure 2 showed the concept of color tuning by the control of the electron-accepting ability depending on substituent at carbon atom linked to the strong electron-withdrawing cyano group.

In our previous works which were studies on red OLEDs and dependence of fluorescence quenching upon molecular structure, some optoelectronic properties of ABCV-Th and ABCV-P were reported.[20–22] As discussed previously, ABCV-P, ABCV-Np and ABCV-Th were designed to prevent concentration quenching and Figure 3 showed the PL emission spectra of them in powder. Unlike

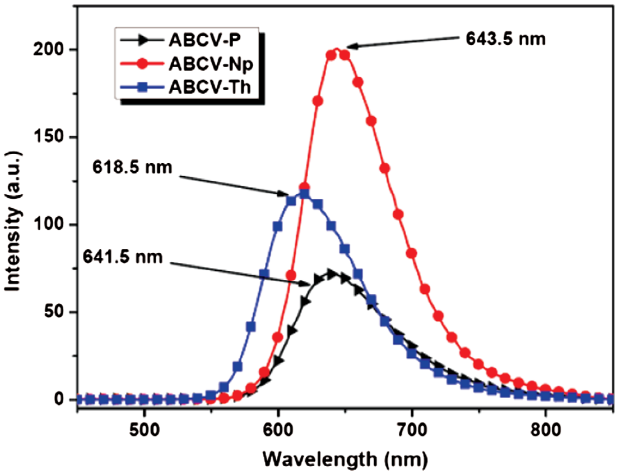


Fig. 3. PL spectra of ABCV-P, ABCV-Np and ABCV-Th excited at 340 nm in powder.

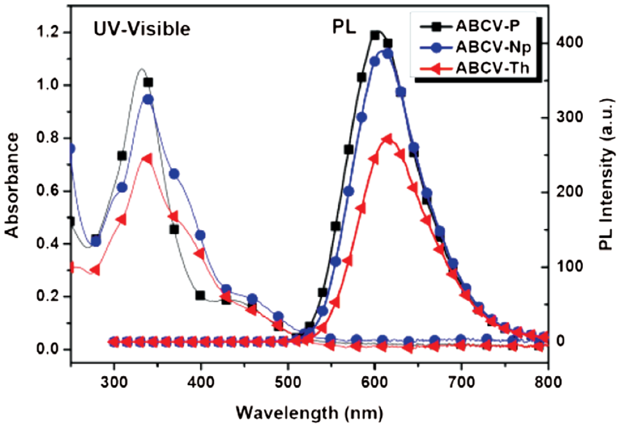


Fig. 4. UV-Visible absorption and PL spectra of ABCV-P, ABCV-Np and ABCV-Th in chloroform (1×10^{-5} M).

typical red dopants, such as DCM2 and DCJTB, their bright PL emissions were observed. The PL emission spectra of them well elucidated that the serious fluorescent concentration quenching due to molecular polarity and planarity doesn't exist any more in these fluorescent molecules.

Figure 4 showed the UV-Visible absorption and PL emission spectra of ABCV-P, ABCV-Np and ABCV-Th in chloroform (1×10^{-5} M). The PL emission spectra of ABCV-P, ABCV-Np and ABCV-Th exhibited large Stokes shifts due to considerable bathochromic shifts in emission wavelengths, which were attributed to the presence of photo-induced ICT excited states[23–25] in the molecules. Owing to the large Stokes shifts, there is hardly an overlap between absorption and emission of light by the ABCV-P, ABCV-Np and ABCV-Th molecules. This leads to little self-absorption of the emitted light so that the fluorophores are advantageous for OLED application.

Figure 5 showed UV-Visible absorption spectra of ABCV-P, ABCV-Np and ABCV-Th in solution (1×10^{-5} M) with variation of solvent polarity. n-Hexane/$CHCl_3$ (99/1) was regarded as "an approximately nonpolar solvent system" in that measurement because these fluorescent compounds insoluble in absolute n-Hexane.

As shown in Figure 5, UV-Visible absorption band of ABCV-Th was shifted to red with increase of solvent polarity. Those shifts of ABCV-P and ABCV-Np were also observed but the magnitude of shifts was smaller compared to that of ABCV-Th. Furthermore, the degree of shifts of absorption bands was very small for all these fluorescent compounds. This low influence of solvent polarity on UV-Visible absorption spectra was interpreted as the ground states of these compounds were not almost affected by the solvent polarity.

Figure 6 showed the effect of solvent polarity on fluorescence emission spectra for ABCV-P, ABCV-Np and ABCV-Th and their peak wavelengths of emission with variation of solvent polarity were summarized in Table I.

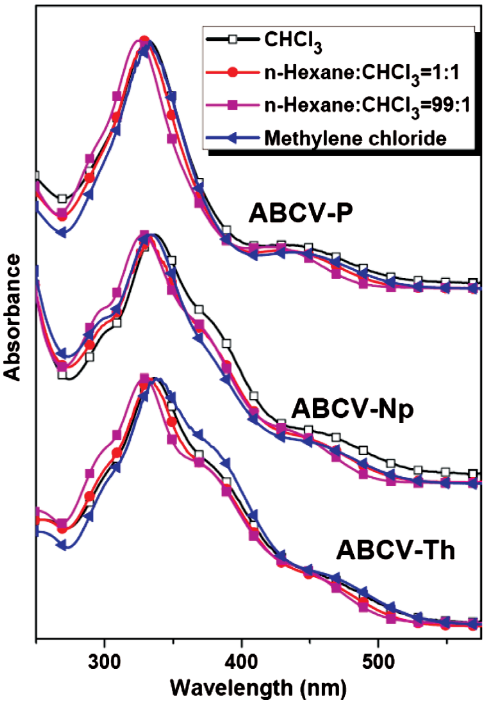


Fig. 5. Normalized UV-Visible absorption spectra of ABCV-P, ABCV-Np and ABCV-Th in solution (1×10^{-5} M) with variation of solvent polarity.

As shown in Figure 6, fluorescence emission spectra of ABCV-P, ABCV-Np and ABCV-Th were dramatically shifted to red as increasing the solvent polarity. As previously discussed, UV-Visible absorption spectra of these fluorophores are not almost affected by variation of solvent polarity and, therefore, this suggests an ICT character is associated with excited states of these fluorescent compounds. The fluorescence emission maxima of ABCV-P, ABCV-Np and ABCV-Th in approximately nonpolar solvent (n-Hexane/Chloroform = 99/1) were measured to be

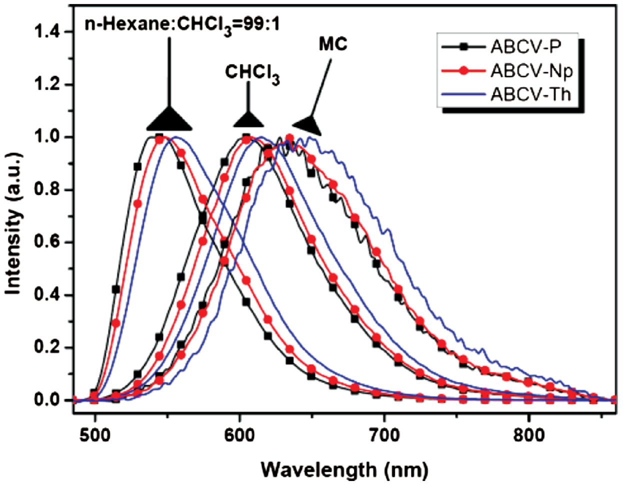


Fig. 6. Normalized PL spectra of ABCV-P, ABCV-Np and ABCV-Th (1×10^{-5} M) with variation of solvent polarity.

Table I. Fluorescence emission maxima of ABCV-P, ABCV-Np and ABCV-Th in solution (1×10^{-5} M) with various solvent polarity.

	$\lambda_{\max}^{\text{flu}}$ (nm)		
Solvent	ABCV-P	ABCV-Np	ABCV-Th
n-Hexane/chloroform (99:1)	539.0	548.5	555.5
n-Hexane/chloroform (1:1)	585.5	592.5	601.0
Chloroform	605.0	608.0	615.0
Methylene chloride	628.0	634.0	648.5

539.0, 548.5 and 555.5 nm, respectively. In this nonpolar solvent, locally excited (LE) states of these compounds would be the lowest excited energy states and, thus, those emission maxima were approximately originated from LE emissions for them, respectively.

As shown in Figure 2, these fluorescent compounds all have the same electron-donating group (*N*,*N*-dimethylamino group) and, thus, the controlling the degree of ICT would be carried out by variation of substituents, such as phenyl, 2-naphthyl and 2-thenyl, at the carbon atom linked to electron-withdrawing cyano group. In Figure 6, fluorescence emission maxima of ABCV-P, ABCV-Np and ABCV-Th in chloroform ($\mu m = 1.1$ D)[26] were measured to be 605.0, 608.0 and 615.0 nm, respectively. In methylene chloride ($\mu m = 1.8$ D),[26] the more polar solvent, those emission maxima were strongly red-shifted to 628 (ABCV-P), 634 (ABCV-Np) and 648.5 nm (ABCV-Th), respectively. This result indicates that ICT states of ABCV-P, ABCV-Np and ABCV-Th are more stabilized by polar solvent than nonpolar solvent and become the lowest excited energy states and, thus, the larger bathochromic shifts of emission spectra are observed. In methylene chloride (1.8 D), the more polar solvent, fluorescence emission peak wavelengths were shifted to longer wavelengths by 23.0 (ABCV-P), 26.0 (ABCV-Np) and 33.5 nm (ABCV-Th), respectively, with respect to those in chloroform (1.1 D), the less polar solvent. This indicates that the decreasing order of the magnitude of ICT is ABCV-Th (2-thienyl), ABCV-Np (2-naphthyl) and ABCV-P (phenyl). Therefore, this supported that fluorescence emission wavelengths of these compounds could be tunable to a various range of red-light emission by variation of substituent at the carbon atom bonded to electron-withdrawing cyano group.

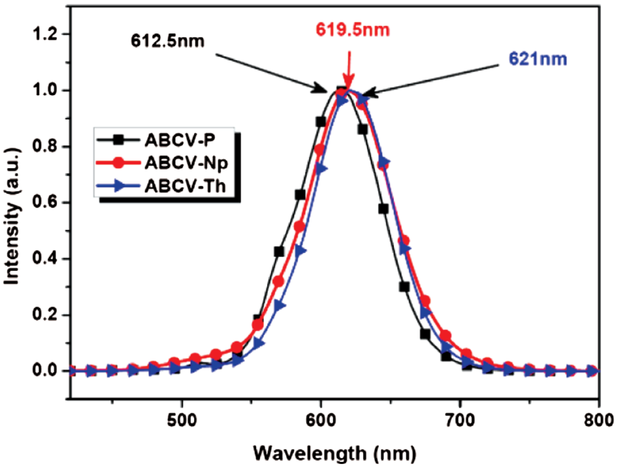


Fig. 7. Normalized EL spectra of ABCV-P, ABCV-Np and ABCV-Th with the device structures of ITO (100 nm)/NPB (40 nm)/red emitters (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm), in which red emitters are ABCV-P, ABCV-Np and ABCV-Th.

Figure 7 showed electroluminescence (EL) emission spectra of OLEDs with the device structures of ITO/NPB (40 nm)/red emitters (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al, in which red emitters were ABCV-P, ABCV-Np and ABCV-Th, respectively. EL emission spectra of ABCV-P ($\lambda_{\max} = 612.5$ nm), ABCV-Np ($\lambda_{\max} = 619.5$ nm) and ABCV-Th ($\lambda_{\max} = 621.0$ nm) also showed the similar tendency to PL emission spectra of them.

4. CONCLUSION

In conclusion, we synthesized red fluorescent compounds, ABCV-P, ABCV-Np and ABCV-Th, which were designed to prevent fluorescence concentration quenching and to have ICT character, and measured their optoelectronic properties to investigate substituent effect on tuning of photoluminescence and electroluminescence emission colors in these compounds. Measurement of UV-Visible absorption and PL emission spectra of these fluorophores with variation of solvent polarity supported that these fluorescent compounds possessed ICT characters. The degree of ICT with variation of substituent at the carbon atom bonded to electron-withdrawing cyano group for this molecular system could be also evaluated by measurement of PL emission spectra in various solvent. As the magnitude of ICT was increased, the larger Stokes shift was generated and, thus, PL emission was shifted to a longer wavelength. The result from measurement of EL emission spectra was well correlated with that of PL emission spectra. Therefore, it is concluded that, in this molecular system, adjustment of electron-withdrawing ability by variation of substituent would become a good tool for tuning of PL and EL emission color of these fluorescent compounds.

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