Chinese Chemical Letters Vol. 15, No. 3, pp 375-378, 2004
http://www.imm.ac.cn/journal/ccl.html

Synthesis of New Naphthaline-type Chromophores with Strong Green-emitting or the Blue-emitting in β-Cyclodextrin

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Abstract: Three new naphthaline-type chromophores end-capped with different (*p*-substituted amino) styryl groups on the both sides (named as BPASN, BHMASN and BMASN) have been synthesized. Under excitation of 380 nm, strong green light-emitting locating at 517 nm with the fluorescence quantum yield of 0.88 in CH_2Cl_2 has been obtained. In the presence of β-cyclodextrin (β-CD), strong blue-emitting at 456 nm in DMF was also recorded.

Keywords: (*E*)-1,4-Bis[p-pyrrolidinylstyryl]naphthalene, (*E*)-1,4-bis[*p*-(N-hydroxyethyl-N-methyl-amino) styryl]naphthalene, (*E*)-1,4-bis[*p*-di(methylamino)styryl]naphthalene, photoluminescence, β-cyclodextrin.

Recently, molecular two-photon absorption (TPA) has found new applications of up-conversion[1], and two-photon excited fluorescence microcopy[2]. Materials used in these applications generally possess two characters: high two-photon absorption cross section and high two-photon excited fluorescence quantum yield, the latter relies on high one-photon fluorescence. Molecular two-photon luminescence and the one-photon luminescence have some similarity[3]. In addition, we have found that some symmetrical substituted stilbenes end-capped with the electron-releasing groups display strong one-photon excited fluorescence[4]. Following the previous work we report here three new symmetrically substituted molecules that are naphthaline-type chromophores bearing different substituted amino-styryl groups on the terminals. The newly synthesized chromophores are shown in **Figure1**. Extraordinarily strong green light-emitting has been observed in solution and in PMMA film, while in the presence of β-cyclodextrin (β-CD), strong blue-emitting was recorded. The structural feature of the rigid naphthaline ring, the conjugated length extended and the symmetrical substituted molecule may be accountable for these results.

Experimental

IR spectra, nuclear magnetic resonance spectra and mass spectra were measured on a Nicolrt FT-IR 5DX, GCT-TOF and INOVA400 instruments, respectively. Differential

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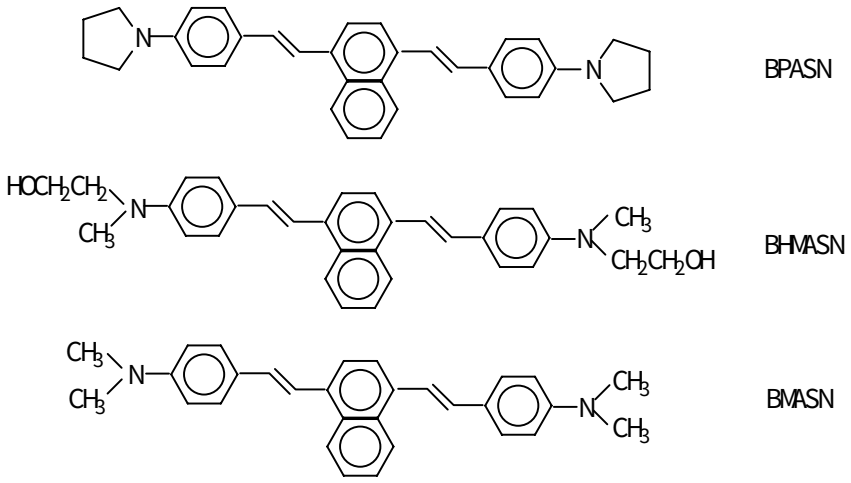
Figure1 The newly synthesized molecular structures



scanning calorimetry (DSC) was carried out at the heating rate of 10^0C/min under nitrogen atmosphere. Absorption spectra of all chromophores in CH_2Cl_2 at 1.0×10^{-5} mol/L have been measured in quartz cuvettes of 1 cm path on UV-Vis TU-1800 recording spectrophotometer. Photoluminescence spectra were measured on an Edinburgh FLS920 spectrometer (All the slits are 1mm).

(*E*)-1,4-Bis[p-pyrrolidinylstyryl] naphthalene (BPASN): A flask fitted with magnetic stirrer and condenser was charged with 6.3 g (0.02 mol) 1,4-di(bromomethyl) naphthalene, then 5.5 g (0.021 mol) of triphenylphosphine and 100 mL fresh distilled xylene. The reaction was refluxed for 4 hours, then cooled to room temperature and filtered. The white powder was recrystallized from ethanol to give colorless crystals 1,4-di(methylene triphenyl phosphonium bromide) naphthalene **1**.

Under anhydrous and oxygen-free conditions, a solution of 11 g (0.1 mol) of potassium *tert*-butoxide in *tert*-butyl alcohol was added by a dropping funnel into a flask in the presence of 5.3 g (0.03 mol) 4-pyrrolidinobenzaldehyde[1] and 4.7 g (0.015 mol) of **1** in 100 mL dry THF solution in ice cooling. After finishing the addition, the mixture was refluxed for 40 hours at room temperature. Then the reaction mixture was cooled to room temperature, poured into warm water, neutralized with dilute hydrochloric acid, extracted with chloroform, and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, and the residua were purified by column chromatography. 3.1g orange crystals (BPASN**)** were obtained, yield 44%, mp 151^0C. ν (KBr)/cm^{-1} 3054.61, 2923.75, 2855.26, 1663.90, 1596.77, 1521.52, 1436,62, 1184.80, 1119.81, 997.23 (*trans*-CH=CH). Mass spectrum：*m/z* 470.26 (M^+), 400.19, 315.16, 234.62. ^{1}H NMR ($CDCl_3$, ppm): δ 1.224-1.259 (m 2H×4, $NCH_2CH_2CH_2$), 3.696-3.745 (t, 2H×4, *J*=6.5 Hz, $NCH_2CH_2CH_2$), 7.271-7.692 (m, 18H, Ar-H, and vinylic H).

Following the same method described above, (*E*)-1,4-bis[*p*-(N-hydroxyethyl-

N-methylamino)styryl] naphthalene, (BHMASN) and (*E*)-1,4-bis[*p*-di(methylamino) styryl] naphthalene (BMASN) were obtained just adding 4-(N-hydroxyethyl-N-methyllamino) benzaldehyde[1] or dimethylaminobenzaldehyde to the flask in the place of 4-pyrrolidinobenzaldehyd.

BHMASN: orange powder. Yield 64%. ν (KBr)/cm^{-1} 3027.03, 2923.25, 2863.16, 1603.78, 1519.81, 1374.55, 1187.40, 1119.76, 962.07 (*trans*-CH=CH). Mass spectrum：*m/z* 478.26 (M^+), 460.22, 448.23, 433.22, 418.23, 403.21, 315.15, 277.18, 209.11. ^{1}H NMR ($CDCl_3$, ppm): δ 3.135 (s, 3H×2, N-CH_3), 3.37-3.397 (t, 2H×2, *J*=5.4 Hz, N-CH_2-), 3.712-3.735, (t, 2H×2, *J* 4.6 Hz, -CH_2-O-), 7.485-8.169 (m, 18H, Ar-H, and vinylic H).

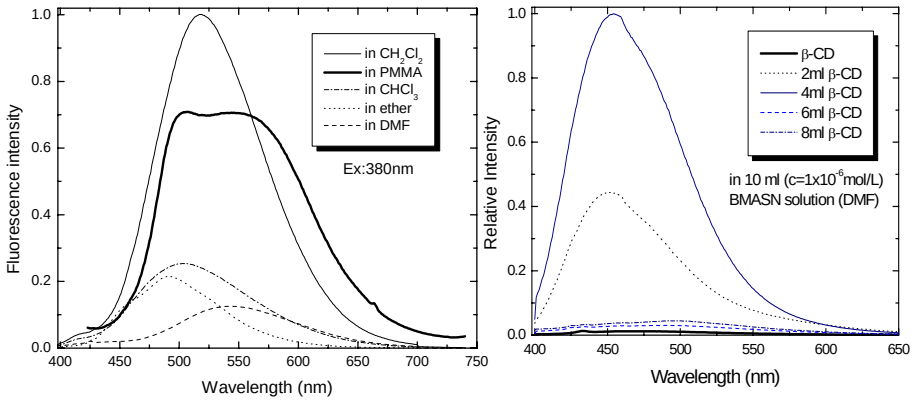
BMASN: orange crystals. Yield 89% and T_{gl}:136℃. ν (KBr)/cm^{-1} 3057.75, 2919.49, 1613.83, 1523.73, 1436.18, 1185.52, 1120.14, 997.09 (*trans*-CH=CH). Mass spectrum：*m/*z 418.24 (M^+), 403.21, 388.19, 374.18, 296.13, 277.18, 218.56, 209.16. ^{1}H NMR ($CDCl_3$, ppm): δ 3.015 (3H, s, N-CH_3), 7.265-7.896 (m, 18H, Ar-H, and vinylic H).

Optical Properties

Electronic absorption spectrum of BMASN showed an absorption band at 380 nm in CH_2Cl_2 (ε_{max}=3.99×10^4L/mol·cm) at the concentration of 1×10^5mol/L. Under excitation of 380 nm, the photoluminescence spectra for BMASN in different solvents at c=1×10^5mol/L and in PMMA film (~2 μm thick) coating on ITO glass were presented (see **Figure 2**).

Figure 2 Emission spectra of BMASN in BMASN in different solvents and PMMA film.

Figure 3 fluorescence spectra of the presence of β-CD



One can see that the emission peak is red-shifted with the increase of solvent polarity. For example, the maximum fluorescence peak shifts from 490 nm in diethyl ether (E_T(30)[5], 34.6), 504 nm in chloroform (E_T(30), 39.1), 517 nm in dichloromethane (E_T(30), 41.1) to 545 nm in DMF (E_T(30), 43.8). On the other hand, the relative fluorescence intensities in CH_2Cl_2 and in the film are much higher than those in other solvents. The photoluminescence quantum yield (Φ) for the green light-emitting in

CH_2Cl_2 in **Figure 2** was calculated to be 0.88 referenced to quinine sulfate (0.53)[6].

Figure 2 displays the photoluminescence of BMASN solution (DMF 1×10^{-6} mol/L) in the presence of β-CD (DMF 1×10^{-2} mol/L). It is interest that a new strong blue-emitting at ~450 nm appears, meanwhile the normal fluorescence of 545 nm (also see **Figure 2**) is quenched. And this blue fluorescence intensity increases at the ratio 1:5:11 with the amount of β-CD from 0 mL, 2 mL to 4 mL in BMASN solution. This strongly suggests that BMASN transfers from the polar environment (DMF) to the less polar environment (β-CD), which avoids the intramolecular twisting responsible for the stabilization of the "TICT" state. The relative fluorescence intensity of BMASN is dramatically decreased when the amount of β-CD is increased to 6 mL or 8mL, presumably because of the dilutedness by β-CD. Detailed optical properties for BPASN, BHMASN and BMASN will be reported later.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 50273024), and the Natural Foundation of Jiangsu Province (Grant No. BK2002041) and the Foundation of Jiangsu Province Education Committee (Grant No. 02KJB430001).

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Received 19 February, 2003