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Synthesis and characterization of a new chromophor with acid/base-sensitive fluorescence emission

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Abstract

A new two-photon absorption compound, 2-{4-[(dicyanomethylidene-5,5-dimethylcyclohexl)vinyl]phenyl}imidazo[4,5-f][1,10]phenanthroline (DDVPIP), was synthesized and characterized. The one-photon excited fluorescence (OPEF) and two-photon excited fluorescence (TPEF) of DDVPIP are sensitive to the acid/base of the solution, which are enhanced in basic solution but weakened in acidic solution. Charge-transfer (CT) states of DDVPIP were calculated through theory methods to explain its acid/base-sensitive fluorescent properties.

Keywords: Imidazo[4,5-f][1,10]phenanthroline; Two-photon absorption; Two-photon fluorescence

Organic materials that can simultaneously absorb two photons have been extensively studied due to their increasing applications in optical power limiting, two-photon upconverted lasing, confocal imaging, photodynamic therapy, and three-dimensional optical data storage [1,2]. An important addition to those applications would be the development of two-photon sensors for biological applications [3,4]. Imidazo[4,5-f][1,10]phenanthroline (abbreviated as IP) derivatives and its metal complex has been demonstrated to be good emitters with interesting proton induced on-off emission switching characteristics through a reversible acid/base interconversion of imidazole group [5–8]. On the other hand, the isophorone-based dopant is an excellent red fluorescent material for organic light-emitting device (OLED) [9,10]. Here, a compound containing IP and isophorone was designed, which might be expected to be a fluorescent pH sensor.

1. Experimental

The compounds 1,10-phenanthroline-5,6-dione [11], 2-(4-formylphenyl)imidazo[4,5-f][1,10]phenanthroline (fmp) [12], dicyanomethylidene-isophorone [9] were synthesized according to the literature methods. All other reagents were obtained commercially and used as supplied (see Scheme 1).

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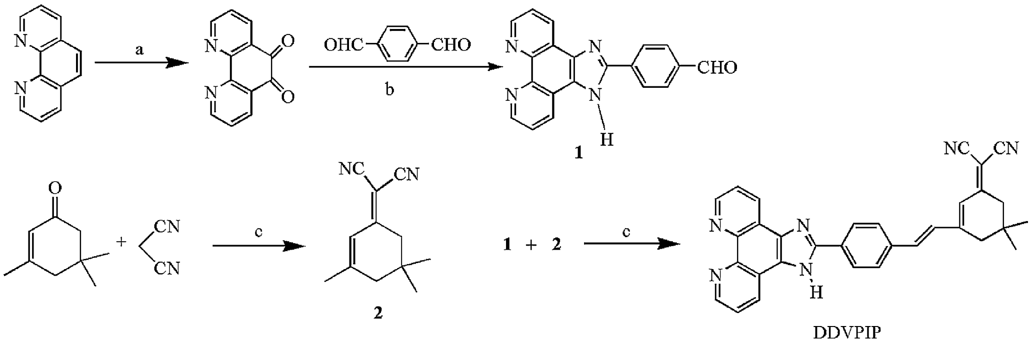

Scheme 1. Regents and conditions: (a) $H_2SO_4/HNO_3/KBr$, reflux, 2 h, 95%; (b) NH_4Ac/CH_3COOH, reflux, 3 h, 70%; (c) $CH_3COOH/C_5H_{10}N$, DMF/benzene (90% for **2**, 32% for DDVPIP).

^1H NMR and ^{13}C NMR spectra were recorded on Bruker A Vance 400 MHz instrument. The electrospray mass spectrum (ES-MS) was determined on an ABI 4000 mass spectrograph. The liner absorption spectra were recorded on a TU-1800 SPC spectrophotometer. OPEF spectra were obtained on an Edinburgh FLS920 spectrofluorometer. The fluorescence quantum yields Φ_F was determined by the method in the reference with Cormarin 307 in methanol ($\Phi_F = 0.57$) was adopted as a reference [13]. TPEF spectra were noted on an OOIBASE32 spectrophotometer. The pump laser beam came from a mode-locked Ti:sapphire laser system, pulse duration 200 fs, repetition rate of 76 MHz (Coherent Mira900-D). TPA cross-section (σ) was measured using two-photon-induced fluorescence measurement technique [14] and fluorescein in water with pH 11 was selected as the standard ($\sigma = 36$ GM) [15].

2-(4-Formylphenyl)imidazo[4,5-f][1,10]phenanthroline (fmp) 3.24 g (0.01 mol) and dicyanomethylidene-isophorone 1.86 g (0.01 mol) were dissolved in 40 mL DMF, and 1 mL hexahydropyridine ($C_5H_{10}N$), 1 mL glacial acetic acid (CH_3COOH) were added to the solution respectively. Stirring was continued for 1 h at room temperature during which the reaction mixture become to red slowly. Then 100 mL dry benzene was added and the reaction mixture was heated under reflux for 8 h. After benzene was distilled off, the residual reaction mixture was cooled to room temperature and 200 mL water was added, many precipitate was formed. The precipitate was collected through filtration and recrystallized from ethanol to give red crystals of DDVPIP (1.57 g, 0.0032 mol, 32%). Mp: 154 °C. ^1H NMR (400 MHz, TFA): δ 9.50 (d, 2H), 9.30 (d, 2H), 8.34 (q, 2H), 8.18 (d, 2H), 7.87 (d, 2H), 7.27 (q, 2H), 7.01 (s, 1H), 2.67 (s, 2H), 2.56 (s, 2H), 1.09 (s, 6H). ^{13}C NMR (100 MHz, TFA): δ 25.49, 31.23, 38.05, 42.39, 75.83, 119.21, 124.33, 124.88, 126.61, 127.79, 128.39, 132.68, 134.44, 135.62, 136.34, 142.50, 146.77, 150.55, 155.86, 173.94. ES-MS (M^++H) *m/z* (%): Calcd. for $C_{32}H_{24}N_6$ 493.7, Found 493.7 (100%).

2. Results and discussion

Variations of liner absorption, OPEF and TPEF spectra of DDVPIP due to acid/base changes were investigated in mixed neutral solvent: THF/H_2O, acidic solvent: THF/0.1 mol/L HCl aqueous solution and basic solvent: THF/0.1 mol/L NaOH aqueous solution. The mixed ratio in three solvents was 9:1 (v/v). The liner absorption, OPEF and TPEF spectra of DDVPIP in neutral, acidic and basic solvents were shown in Fig. 1.

As shown in Fig. 1(a), in the neutral THF/H_2O, there was one strong absorption band with maxima peak located at 433 nm. But in basic solution, the whole absorption spectra became featureless and much broader with the longer wavelength absorption was increased while the shorter wavelength absorption was reduced. In the acidic solution, the maxima peak located at 413 nm and the spectral profile was not changed compared with in neutral solution. As shown in Fig. 1(b), in the neutral THF/H_2O, excited by 360 nm wavelength, DDVPIP emission fluorescence with maxima peak located at 571 nm. The Φ is 0.27. Compared with neutral solution, the maxima peak of DDVPIP in basic solution underwent a blue shift and the strength was enhanced, Φ increased to 0.53. While in acidic solution, the OPEF spectra were vanished significantly, Φ decreased to 0.056. As shown in Fig. 1(c), a similar change of TPEF of DDVPIP took place as that of OPEF in these solvents. In the neutral THF/H_2O, excited by 800 nm wavelength, DDVPIP emission two-photon fluorescence with the maxima peak at 615 nm, which TPA cross-section was obtained as 46 GM. Compared with neutral solution, the TPEF of DDVPIP in basic solution was intensified and its maxima peak located at