Synthetic Metals 161 (2011) 354–359

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Synthesis and photophysical properties of a new two-photon absorbing chromophor containing imidazo[4,5-*f*][1,10]phenanthroline

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ARTICLE INFO

Article history:
Received 12 October 2010
Received in revised form
23 November 2010
Accepted 1 December 2010
Available online 19 December 2010

Keywords:
Imidazo[4,5-*f*][1,10]phenanthroline
Two-photon absorption
Two-photon fluorescent sensor

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. Its two-photon absorption (TPA) cross-section is obtained as 62 GM ($1\,GM = 1 \times 10^{-50}\,cm^4\,photon^{-1}\,molecule^{-1}$) with 200 fs laser pulses at 800 nm. 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 the 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.

1. Introduction

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 [1–3]. An important addition to those applications would be the development of two-photon sensors for biological applications [4]. It is well known that one of the major drawbacks of one-photon fluorescent sensors is that the excitation wavelengths are within the range of 350–560 nm, which may cause damages to the substrates [5,6]. This problem could be avoided if two-photon sensors are used, because the chromophore could maintain a significant two-photon excited fluorescence (TPEF) action cross-section in the range of 700–1000 nm, which is a suitable excitation window for biological imaging. Then, two-photon laser scanning microscopy (TPLM) [7] with suitable two-photon chemosensors can image the distribution of the guest molecules and ions in living cells with much less photodamage than that caused by the one-photon technique [8,9]. However, there are only limited applications of two-photon sensors for metal ions, fluoride ions, and pH which have been studied in organic solvents or model membranes [10–18]. Thus, it will be of great importance to develop such sensors.

Imidazo[4,5-*f*][1,10]phenanthroline (abbreviated as IP) derivatives and its metal complex are candidates for the third-order NLO materials in virtue of their high harmonic generation and rapid response [19–21]. The complex with imidazole rings uncoordinated to the Ru(II) center 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 [22–27]. IP derivatives and their metal complex may be expected to be TPEF-optimized molecular sensors to the pH of solution. On the other hand, the isophorone-based dopant is an excellent red fluorescent material for organic light-emitting device (OLED) [28–31]. Synthesis as well as understanding the photophysical properties and functions of new isophorone-based materials is still crucial for their exploration and applications. Here, a compound containing IP and isophorone was designed, which might be expected to be a fluorescent pH sensor, with promising applications in the field of electroluminescent (EL) materials and organic light-emitting device (OLED).

In this article, the target compound, 2-{4-[(dicyanomethylidene-5,5-dimethylcyclohexl)vinyl]phenyl}imidazo[4,5-*f*][1,10] phenanthroline (DDVPIP), was synthesized and characterized. Its liner absorption, OPTF and TPEF in response to changes in acid–base of the solutions were studied, and the charge-transfer (CT) states of the compound were calculated using theory methods.

2. Experiments

2.1. Instrument and physical measurements

Nuclear magnetic resonance spectra were obtained on Bruker Avance 400 spectrometer. Elemental analysis was performed using

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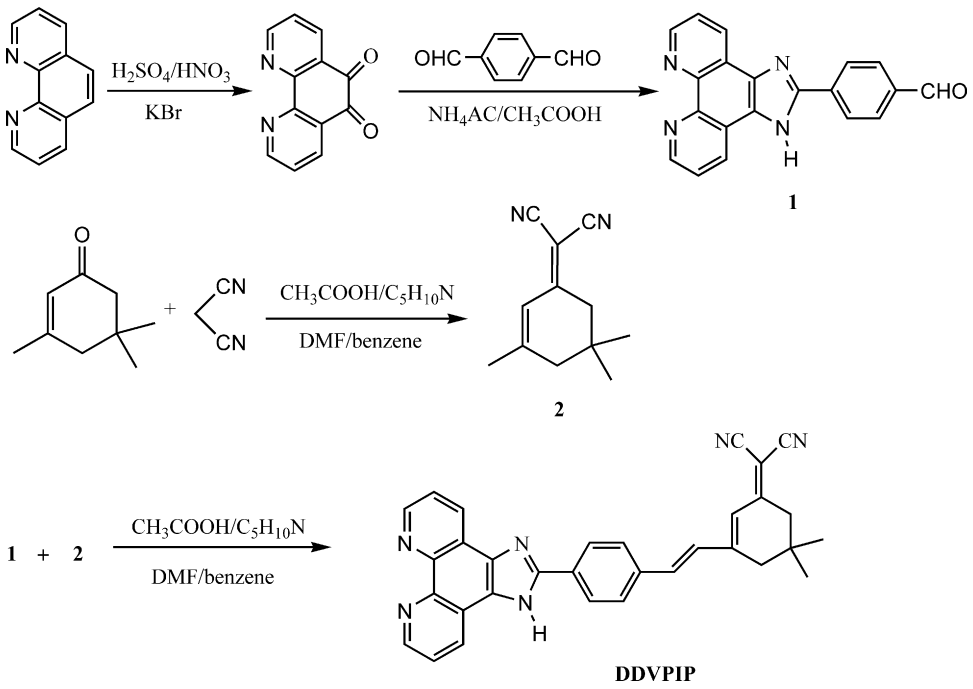
0379-6779/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.synthmet.2010.12.003



Scheme 1. The synthesis and chemical structure of DDVPIP.

Vario. ELIII (German) elemental analyzer. The electrospray mass spectrum (ES-MS) was determined on an ABI 4000 mass spectrograph. The diluted solution was electrosprayed with a needle voltage of +5.5 kV. The mobile phase was an aqueous solution of methanol (V/V, 1:1). Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. The samples were prepared as KBr pellets. Melting point is measured on DSC822e Mettler-Toledo instruments.

The liner absorption spectra of dilute solutions were recorded on a TU-1800 SPC spectrophotometer using a quartz cuvette having 1 cm path length. OPEF spectra were obtained on an Edinburgh FLS920 spectrofluorometer equipped with a 450 W Xe lamp and a time-correlated single-photon counting card. The fluorescence lifetime measurement was performed on the same spectrofluorometer with a hydrogen flash lamp (pulse duration < 1 ns) as the excitation source. Re-convolution fits of the decay profiles were made with F900 analysis software to obtain the lifetime values. The OPEF quantum yields Φ were determined by the literature method using coumarin 307 as standard, which has the same concentration with the samples as Ref. [32]. 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). All measurements were carried out in air at room temperature. TPA cross-sections were measured using two-photon-induced fluorescence measurement technique [33].

2.2. Chemicals and synthesis

The compounds 1,10-phenanthroline-5,6-dione [34], 2-(4-formylphenyl)imidazo[4,5-*f*][1,10]phenanthroline (fmp) [19], dicyanomethylidene-isophorone [28,29] were synthesized according to the literature methods. All other reagents were obtained commercially and used as supplied (see Scheme 1).

2-{4-[(Dicyanomethylidene-5,5-dimethylcyclohexl)vinyl] phenyl}imidazo[4,5-*f*][1,10]phenanthroline (DDVPIP)

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 becomes 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 precipitates were 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. ^{1}H NMR (400 MHz TFA) δ_H: 9.50 (d, J = 8.41 Hz, 2H), 9.30 (d, J = 5.00 Hz, 2H), 8.34 (q, J = 13.50 Hz, 2H), 8.18 (d, J = 8.27 Hz, 2H), 7.87 (d, J = 8.34 Hz 2H), 7.27 (q, J = 16.15 Hz 2H), 7.01 (s, 1H), 2.67 (s, 2H), 2.56 (s, 2H), 1.09 (s, 6H). ^{13}C NMR (400 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, $C_{32}H_{24}N_6$ (M^++H) m/z (%): calcd: 493.7, found: 493.7 (100%). IR (KBr cm^{-1}): 739 (s), 811 (m), 855 (m), 880 (w), 951(s), 1050 (m), 1158 (m), 1184 (m), 1331(s), 1393 (s), 1524 (s), 1562 (s), 1727 (m), 2217 (s), 2871 (m), 2964 (s), 3734 (s). Element analysis: $C_{32}H_{24}N_6{\cdot}CH_3CH_2OH$ calcd: C, 75.81; H, 5.61; N, 15.60% found: C, 76.11; H, 4.96; N, 16.43%.

3. Results and discussion

3.1. Linear absorption, OPEF and TPEF spectra

The photophysical properties of DDVPIP are summarized in Table 1. The OPEF spectra and its lifetimes (τ) are measured in different solvents with a concentration of $c = 1 \times 10^{-5}$ mol/l, the excited wavelength is 480 nm. From Table 1 can be seen that the liner absorption maxima peak: $\lambda_{max}^{(1a)}$ in different solvents locate at range from 420 to 432 nm and the one-photon fluorescence maxima peak: $\lambda_{max}^{(1f)}$ locate at range from 546 to 576 nm. Figs. 1 and 2 are linear absorption and OPEF spectra of DDVPIP, respectively, which show that the $\lambda_{max}^{(1a)}$s are not significantly different, while the $\lambda_{max}^{(1f)}$s slightly show a red-shift with the increase of the polarity of the solvent. This can be explained by the fact that the excited state of