Journal of Luminescence 194 (2018) 588–593

Contents lists available at ScienceDirect

Journal of Luminescence

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

Two-photon absorption and mechanofluorochromic properties of 1,4-diketo-2,5-dibutyl-3,6-bis(4-(carbazol-N-yl)phenyl)pyrrolo[3,4-*c*]pyrrole

Kai Zhang, Mingshuai Chen, Zhongwei Liu, Shian Ying, Haichang Zhang, Shanfeng Xue, Wenjun Yang*

Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Provincial, Key Laboratory of Rubber-plastics, School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao 266042, China

ARTICLE INFO

Keywords:
Fluorescent DPP derivative
Two-photon absorption
Mechanochromic luminescence
D-π-D molecule
Multifunctional dye

ABSTRACT

A new diketopyrrolopyrrole-based fluorescent dye 1,4-diketo-2,5-dibutyl-3,6-bis(4- (carbazol-N-yl)phenyl)pyrrolo[3,4-*c*]pyrrole (DPPCZ) was synthesized and characterized. DPPCZ with donor–π–acceptor–π–donor motif exhibited large and solvent-dependent two-photon absorption cross sections (δ) and emitted strong two-photon excitation fluorescence. The measured maximal δ values in $CHCl_3$, THF, DMF, and toluene are 750, 610, 600, and 460 g, respectively. While DPPCZ water-dispersions exhibit aggregation-quenched emission to some extent, the pristine powder, the obtained single crystal, and emulsion could still emit the relatively strong fluorescence with the efficiency of 21%, 9.5%, and 24%, respectively. It was found that both yellow and red DPPCZ crystals with weak intermolecular interactions could be ground into an amorphous orange state, and then recovered to the yellow state by thermal annealing and solvent-fuming, affording a new DPP-based mechanofluoro-chromic (MFC) material. Powder X-ray diffraction and differential scanning calorimetry indicated that the phase transition between crystalline and amorphous states upon external stimuli was responsible for the MFC behavior.

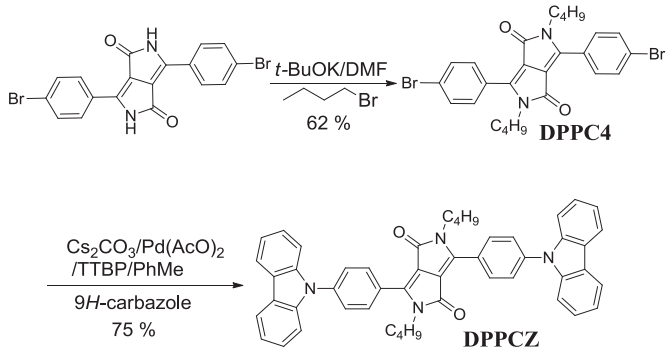
1. Introduction

Great efforts have been devoted to the development of new organic chromophores due to their promising applications in organic light-emitting diodes, field-effect transistors, photovoltaic devices, mechano-, bio- and chemo-sensors. Among them, those derived from common pigments and dyes have attracted special interest since their easier accessibility and chemical modification. Subtle manipulation on molecular structures through chemical and physical methods could further develop their potentials in organic optical, electronic, and optoelectronic fields. In recent years, conjugated organic fluorescent molecules exhibiting large two-photon absorption (2PA) cross sections (δ) and mechanofluorochromic behaviors (MFC) have been receiving much attention. MFC materials involving the physical change of aggregate morphology instead of chemical structure alteration were still isolated events, and it was hard to predict in advance whether a newly synthesized fluorescent molecule could exhibit MFC behavior [1]. Therefore, there was still a great demand for experimental exploitation of new MFC dyes and accumulation of structure–property relationships. 2PA molecules were applicable in two-photon fluorescence imaging, optical power limiting, two-photon up-conversion lasing, three-dimensional (3D) optical data storage, 3D micro-fabrication, and photodynamic therapy [2,3]. The existing studies show that π-center nature, donor/acceptor strength, and linking way among building blocks could significantly influence δ values. The most favored structural motif towards large δ is the donor–π-bridge–acceptor–π-bridge–donor (D–π–A–π–D)-type molecule, and the extensively utilized π-centers are benzene, fluorene, dithienothiophene, biphenyl, benzothiazole, dihydrophenathrene, anthracene, and pyrazine, etc.

1,4-Diketo-pyrrolo[3,4-*c*]pyrrole (DPP) derivatives represent a class of brilliant red high-performance pigments with exceptional light, weather and heat stability [4,5]. It has been known that insoluble DPP pigments could be changed into the soluble dyes with high fluorescence efficiency (Φ) in common organic solvents by introducing mono- and dual alkyl chains on the lactam unit to eliminate strong intermolecular hydrogen bond interactions [6,7]. Up to now, the alkylated DPP derivatives have been extensively used as the building blocks to construct promising conjugated small molecules and polymers applicable in field-effect transistors and photovoltaic devices [8–18], in contrast, the reports on their 2PA and other optical properties are still limited [19–26]. Recently, we and others have found that alkylated simple DPPs themselves could exhibit commendable two-photon activity, and donor-capping could greatly increase 2PA cross sections of DPP derivatives [27–39]. DPP has become a novel and efficient acceptor-type π-center

* Corresponding author.
E-mail addresses: sfxue@qust.edu.cn (S. Xue), ywjph2004@qust.edu.cn (W. Yang).

http://dx.doi.org/10.1016/j.jlumin.2017.09.018
Received 26 April 2017; Received in revised form 7 August 2017; Accepted 8 September 2017
Available online 09 September 2017
0022-2313/



Scheme 1. The synthesis and structure of DPPC4 and DPPCZ.

for constructing organic chromophores with high light- and heat-stability, large δ and strong 2PEF. On the other hand, we consider that the peripheral groups and their linking way to DPP core should affect the aggregation and stimuli-responsive behaviors of DPP-based derivatives. This could provide an opportunity to develop high-performance and multifunctional DPP-based fluorophores [26,40–44]. Herein we employ carbazol-N-yl as end donor unit linking at the *p*-phenyl position of 1,4-diketo-2,5-dibutyl-3,6-diphenylpyrrolo[3,4-*c*]pyrrole to form a new D–π–A–π–D-type molecule (DPPCZ, Scheme 1). We now report that fluorescent DPPCZ exhibits not only large and solvent-dependent 2PA cross sections but also two different crystalline states and obvious mechanofluorochromism. This work has demonstrated again that changing the peripheral groups can indeed affect the aggregation behaviors and optical properties of the DPP-based dyes, providing an approach to developing new DPP-based multifunctional dyes.

2. Experimental section

2.1. Materials

3,6-Bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione was from previous works [28,40]. Toluene (PhMe) and tetrahydrofuran (THF) over metallic sodium, and *N,N*-dimethylformamide (DMF) and chloroform ($CHCl_3$) over calcium hydride were distillated before use. 9-*H*-carbazole, palladium acetate, tri(t-butyl)phosphine (TTBP), potassium *tert*-butoxide (*t*-BuOK), 1-bromobutane (C_4H_9Br), and cesium carbonate (Cs_2CO_3) were obtained from Energy Chemical Ltd. Shanghai, China, and used without further purification. The other solvents were of analytical grade and obtained commercially from available resources.

2.2. Sample preparation

Stimuli-responsive experiments: At room temperature, the organic solid was ground on a glass plate using a metal spatula, and then the ground sample was placed into a beaker containing a small amount of dichloromethane for 5 min and the sample was above the CH_2Cl_2 level. The re-grinding experiment was the same as the first grinding, and then the re-ground sample was placed into an oven for 30 min at 200 °C. Meanwhile, the fluorescence photos were photographed under 365 nm UV lamp and emission spectra were recorded. Single crystal was obtained by the solution diffusion method where chloroform was used as the favorable solvent and methanol as the unfavorable solvent. THF/water (1/9) dispersion of DPPCZ (aqueous dispersion) was prepared by slowly adding 1 mL of THF (or DMF) solution of DPPCZ (1.0×10^{-4} M) into 9 mL of distilled water under ultrasound at room temperature. The aqueous emulsion of DPPCZ was prepared by the same procedure, except that 9 mL of water emulsion (0.2% SDS) was used.

2.3. Measurements

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using a Bruker-AC500 spectrometer in $CDCl_3$ at 298 K and tetramethylsilane (TMS) as the internal standard. UV–visible absorption spectra were recorded using a dual-beam grating Hitachi U-4100 absorption spectrometer with a 1 cm quartz cell. The fluorescence emission spectra were obtained by using a Hitachi F-4600 spectrophotometers. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC (204F1) instrument at a heating (or cooling) rate of 10 °C min^{-1}. The thermo- gravimetric analysis (TGA) was performed on a Netzsch (209F1) thermogravimetric analyzer under a nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The solution fluorescence quantum yield was determined by a dilute solution method using fluorescein in water (pH = 11) as the standard [45].

Two-photo absorption cross section (δ) was performed by using a femtosecond Ti: sapphire oscillator (Avesta TiF-100M) as the excitation source. The laser pulses have pulse duration of 80 fs and repetition rate of 84.5 MHz in the wavelength range of 710–1000 nm. The pumping wavelengths were determined by a monochromator- CCD system. The δ of a sample compound (s) can be calculated at each wavelength according to the equation: $\delta_s = [I_s\Phi_r n_r^2 c_r]/[I_r\Phi_s n_s^2 c_s]\delta_r$) with rhodamine B in methanol was used as a reference standard (r) [46]. Where I was the integral area of the two-photon excitation fluorescence; Φ was the fluorescence quantum yield (assuming that Φ was unchanged under both one- and two-photon excitation), n was the refractive index, and c was the number density of the molecules in solution in which both sample and reference were 1.0×10^{-5} M. Single-crystal X-ray diffraction data were collected using a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo Kα radiation. The structure was solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. All the hydrogen atoms of ligands were generated geometrically. CCDC no. 1545251 containing the crystallographic data can be obtained free from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Synthetic procedures and characterization

2.4.1. Synthesis of 2,5-dibutyl-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPPC4)

Under nitrogen atmosphere, a mixture of 1.14 g (2.56 mmol) of 1,4-diketo-3,6-di(bromophenyl)-pyrrolo[3,4-*c*]pyrrole and 0.83 g (7.40 mmol) of *t*-BuOK in 30 mL anhydrous DMF was stirred for 1 h at 120 °C. Then 1.75 g (12.80 mmol) of 1-bromobutane in 5 mL DMF was slowly added to the mixture. The reaction was kept for 24 h at 130 °C. After being cooled to room temperature, the mixture was poured onto water and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$, and the product was separated by silica column chromatography using dichloromethane as the eluent. A yellow solid product was obtained (0.62 g, yield: 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 7.60–7.70 (m, 8H), 3.70 (t, 4H, *J* = 9.3 Hz), 1.52 (m, 4H), 1.22 (m, 4H), 0.86 (t, 6H, *J* = 9.0 Hz).

2.4.2. Synthesis of 2,5-dibutyl-3,6-(9-carbazolylphen)pyrrolo[3,4-c]pyrrole-1,4-dione (DPPCZ)

0.25 g (0.45 mmol) of DPPC4, 0.60 g (3.60 mmol) of 9-*H*-carbazole, 0.44 g (1.35 mmol) of Cs_2CO_3, 10 mg (45 μmol) of palladium acetate, 20 mg (67.5 μmol) of TTBP and 20 mL toluene were added to a 100 mL one-neck flask under nitrogen atmosphere. The mixture was refluxed for 24 h, and then poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed via rotary evaporation. The crude product was purified by silica column chromatography using petroleum ether/CH_2Cl_2 (1/2, v/v) as the eluent to give product as a yellow solid (0.21 g, yield: 75%).