



Dipicolinate as acceptor in D- π -A chromophores: synthesis, characterization and fluorescence following single- and two-photon excitation

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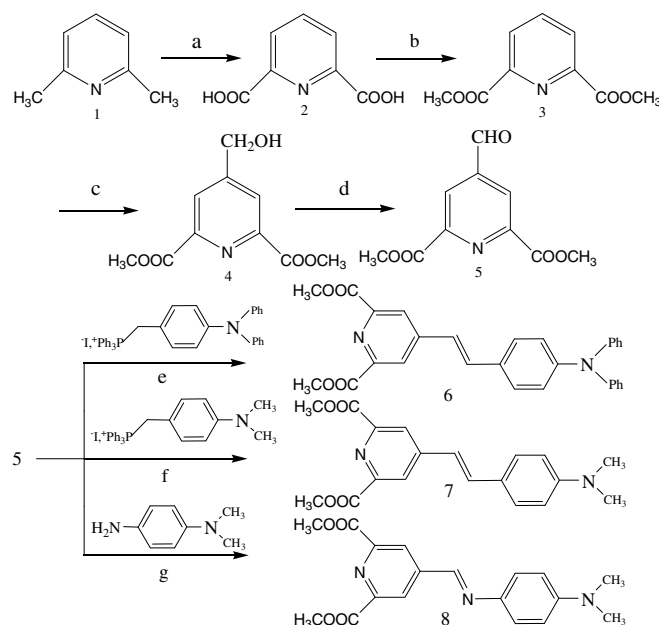
ABSTRACT

Three novel donor- π -acceptor type compounds with dipicolinate as acceptor have been synthesized. Their absorption, photoluminescence as well as their two-photon absorption properties have been investigated. Two of them show strong two-photon absorption and two-photon excited up-conversion fluorescence.

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Research into molecular two-photon absorption (TPA) has received increasing attention owing to numerous applications in various areas such as three-dimensional optical data storage, up-conversion lasing, optical power limiting, microfabrication, photodynamic therapy and two-photon laser scanning fluorescence imaging.^{1–4} Among them, two-photon-excited fluorescence (TPEF) has gained widespread popularity in the biology community owing to its various advantages. The main advantage is that incident wavelengths are located in the region of infrared (700–1200 nm). In this spectral domain, the transparency of biological samples limits absorption and diffusion by the media and thus allows deeper probing (500 μ m). In addition, the bi- or multiphotonic laser excitation is confined in a small focal volume (1 μ m³), which permits 3D resolved imaging while avoiding global irradiation of the sample and thus limiting photodamage to the tissue and photobleaching of the probe. The sensitization of Ln^{III} by two-photon absorption ligand may lead to high-purity Ln^{III} (Eu³⁺, Er³⁺, Nd³⁺, Tb³⁺) emission and less-harmful, deep-penetrating bioimaging applications.^{5–7} Upon the coordination of TPA dyes to metal ions, the mechanical properties and stability in environment of two-photon absorption materials can be improved.^{8–13}

Pyridine-2,6-dicarboxylic (dipicolinic) acid and its derivatives are highly useful tridentate ligands, they can form nine-coordinating complexes with lanthanides.^{14–17} To the best of our knowledge, there has not been any report on dipicolinate and its derivatives as an acceptor in D- π -A chromophores. In this Letter, we describe the synthesis (Scheme 1) and the optical properties (absorption, fluorescence and TPA) of a series of D- π -A chromophores containing dipicolinates. The arylamine group in chromophore functions as an electron donor (D), the dipicolinate moiety acts as an electron acceptor (A) and C=C or C=N double bond as conjugation bridge. Therefore, chromophore is a polar molecule that shows D- π -A



Scheme 1. Reagents and conditions: (a) KMnO₄, H₂O, reflux, 4 h, 80%; (b) CH₃OH, H₂SO₄, reflux, 20 h, 85%; (c) CH₃OH, H₂O₂, FeSO₄, 15–30 °C, 1 h, 30%; (d) CrO₃, pyridine, CH₂Cl₂, 25–30 °C, 5 h, 75%; (e) NaH, THF, rt, 24 h, 50%; (f) NaH, THF, rt, 24 h, 45%; (g) CH₃OH, reflux, 4 h, 85%.

character, which is known to be the structural basis for an efficient two-photon absorber.¹⁸ The structures were determined by ¹H NMR, mass spectrometry, and IR spectrum.¹⁹

The normalized UV-vis absorption spectra of objective compounds **6–8** in CH₂Cl₂ solutions at a concentration of around 1 × 10⁻⁵ M are shown in Figure 1. The maximum peaks of one photon absorption corresponding to π -conjugated structures are at

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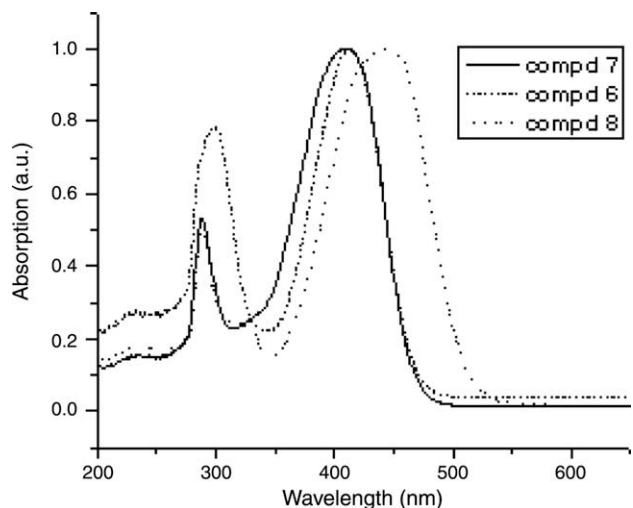


Figure 1. Absorption spectra of compounds **6–8** in CH_2Cl_2 solutions (around 1×10^{-5} M).

413 nm for compound **6** and at 410 nm for compound **7**. Note that the λ_{max} of **7** appears at a shorter wavelength than that of **6**. The result could be explained by noting that the lone pair electrons on the nitrogen of **6** may have delocalized onto the terminal phenyls.²⁰ The maximum UV spectral absorption of compound **8** shifts from 410 nm of **7** to 445 nm when the conjugation bridge varies from C=C to C=N double bond, hinting that the π -electron conjugation bridge has significant effect on their ground state electron absorption spectra of molecules and compound **8** possesses larger π -electron delocalized degree than **7**.²¹ Simultaneously, we found in Figure 1 that compounds **6–8** show absorptions in less than 300 nm wavelength, which are assigned to the $n-\pi^*$ transition. Significantly, compounds **6–8** show no linear absorption in the wavelength range from 500 to 1000 nm. Therefore, any emission induced by excitation at this wavelength range must be attributed to a multi-photon absorption process.²²

Compounds **6** and **7** exhibit green fluorescence in CH_2Cl_2 . As illustrated in Figure 2 for compound **6**, a pronounced positive solvatochromism is observed in emission. A parallel increase of the Stokes shift and of the half bandwidth of the fluorescence spectra is observed. Such behaviour is indicative of significant charge

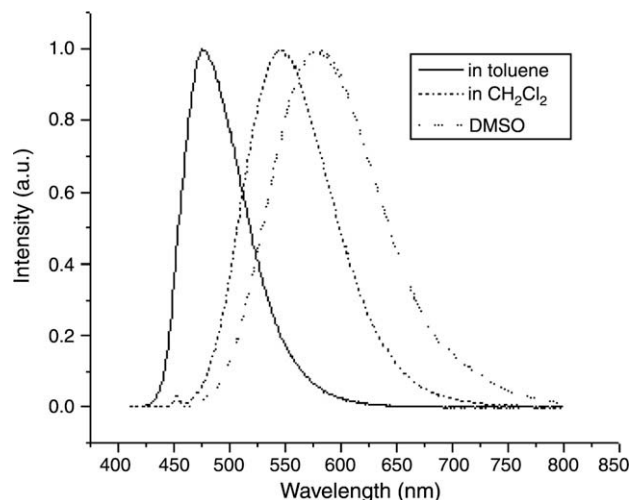


Figure 2. Normalized fluorescence emission spectra of compound **6** in solvents of different polarity.

redistribution occurring upon excitation, prior to emission, and potentially large TPA cross sections.¹ Comparing **6** and **7**, by changing the arylamino in **6** with alkylamino, there is a 12 nm blue-shift in emission spectra. Comparing the structures of **7** and **8**, it can be seen that they are only different from the conjugated bridge. Compound **8** shows very weak emission. The fluorescence quench of **8** may be attributed to the nitrogen atom in the conjugated bridge: (i) The C=N double bond is a polar bond, which may have an effect of reducing charge transfer from donor to acceptor and reduce the molecular polarity. (ii) photoisomerization is one source of nonradiative deactivation.²³ The C=N double bond can be isomerized to the higher-energy and less-stable isomer by irradiating with UV-vis light because of the presence of lone electron pair in nitrogen atom. This photoreaction competes with fluorescence.²³

The TPA induced emission spectra of 10^{-3} M solutions of **6** and **7** in CH_2Cl_2 were detected. When the solutions are pumped with a laser pulse at 800 nm, strong fluorescence emission can be detected. The λ_{max} of the two-photon induced fluorescence for **6** and **7** are at ca. 569 and 551 nm, respectively. The shape are similar to that data obtained by one-photon excitation in the same solvents (Fig. 3). The interesting feature is again the solvatochromism that occurs even on two-photon excitation.

But these fluorescences are red-shifted compared with the one-photon induced fluorescences. The fluorescence spectra in the short wavelength sides and the one-photon absorption spectra in the long wavelength sides overlap. For one-photon absorption induced emission measurements, we used dilute solutions, thus the reabsorption of the fluorescence within the sample can be neglected. In the case of two-photon excitation, concentrated solutions were used. Since the 800 nm laser beam can pass through the whole solution length without depletion, the fluorescence emission is not only from the surface layer, but also from inside the solution sample. The reabsorption of the shorter wavelength fluorescence by the concentrated sample can no longer be neglected. The blue side of the two-photon fluorescence was reabsorbed by the solution and red-shifts of the fluorescence spectra were observed.²² Tian et al.²⁴ reported the synthesis and photophysical properties of 4-[4-(diethylamino)styryl]pyridine (DEASP). We note that the absorption and the fluorescence maximal wavelengths of compound **7** show bathochromic shifts and the Stokes shift increases in comparison to DEASP (Table 1). This spectroscopic behavior reflects the fact that the presence of two electron-withdrawing methoxycarbonyl groups in pyridine ring

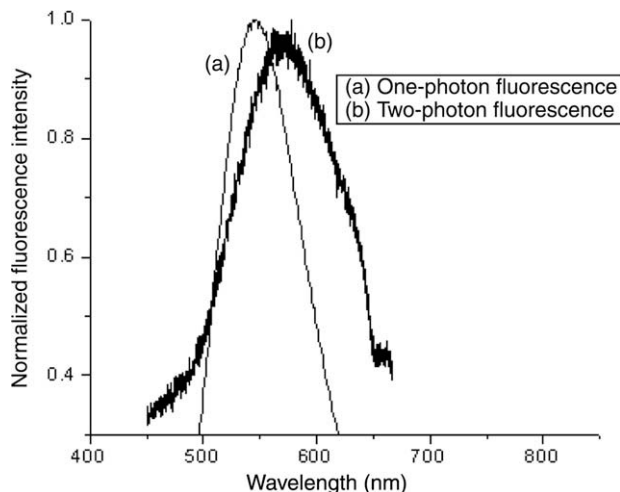


Figure 3. One-photon fluorescence and two-photon fluorescence spectra of compound **6**.

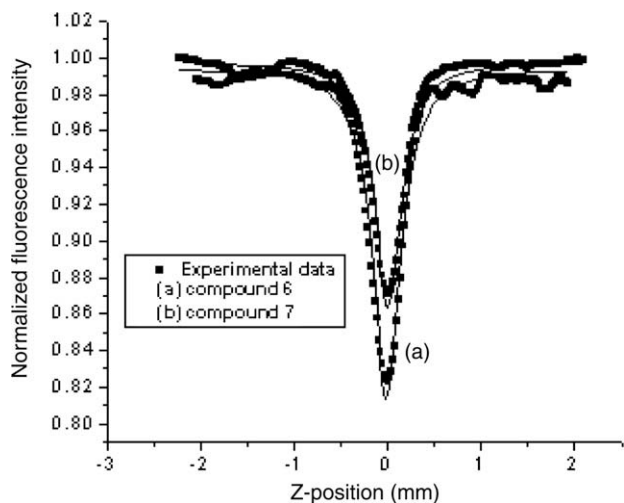
Table 1
Linear absorption and emission parameters of compounds **6**, **7** and DEASP in CH₂Cl₂

Compd	λ_{\max}^a (abs)/nm	λ_{\max}^b (fl)/nm	$\Delta\lambda^c$	ϕ^d	λ_{\max}^e (TPEF)/nm
6	299, 413	544	131	0.85	569
7	290, 410	532	122	0.63	551
DEASP	267, 376.5	464	87.5		480 (in DMF)

^a λ_{\max} of the one-photon absorption spectra in nm.^b λ_{\max} of the one-photon emission spectra in nm.^c Stokes shift.^d Fluorescence quantum yield.^e λ_{\max} of the two-photon absorption spectra in nm.

enhances the acceptor strength and the acceptor stabilizes the lowest excited state more than the ground state.⁸

The TPA cross sections of molecules **6** and **7** have been measured by open aperture Z-scan experiments performed with a femtosecond (fs) laser source. Figure 4 shows the Z-scan data of dyes **6** and **7** in DMSO, measured in a 1 mm cell, with 0.749 μ J pulse. In Figure 4, the normalized transmittance (i.e., $I(z)/I(\infty)$, with $I(\infty)$ being the linearly transmitted intensity far from the focal plane) is reported as a function of the sample position (z). Compounds **6** and **7** show deep dip typical of nonlinear absorption. Table 2 reports the fs TPA cross-section coefficients of compounds **6** and **7** compared to two representative literature examples measured with fs pulses. *N,N*-diphenyl-7-[2-(4-pyridyl)ethenyl]-9,9-di-*n*-decyl-9*H*-fluoren-2-amine (AF50) and (7-(7-benzothiazol-2-yl)-9,9-diethylfluoren-2-yl)-9,9-diethylfluoren-2-yl)diphenylamine (AF250) are two of the most representative TPA dyes so far reported in the literature.²⁵ It can be seen that the TPA cross-section coefficient of **6** is larger than AF50 and **7** is larger than AF250. However, it should be considered that the TPA measurements of **6** and **7** have been carried out at the nonoptimized 800 nm wavelength position. An enhancement of σ value is expected at optimized parameters.²⁵

**Figure 4.** Z-Scan experimental data of compounds **6**(a) and **7**(b) in DMSO (10^{-2} M).**Table 2**
TPA cross-section coefficient of compounds **6** and **7** in DMSO is compared with those of different compounds in the literature data

Compd	Pulse laser		σ [GM]
	λ (nm)	Fwhm (fs)	
6	800	140	35
7	800	140	23
AF50	796	150	22
AF250	796	150	30

It is also interesting to note that σ value increase upon replacing dimethylamino group in compound **7** with diphenylamino group (compound **6**). The result could be explained by noting that²⁰ (i) NPh₂ has a better cation stabilizing ability and (ii) the additional degree of spatial delocalization of the mobile electrons for **6** is possible. To elaborate point (i), it should be noted that the diphenylamino group is a much weaker electron donor than the former, as indicated by the smaller pK_a value of Ph₂NH (0.9) than Et₂NH (10.8) and by the more positive oxidation potential. Hence, the ground state of **6** would be located at slightly lower energy than **7**. On the other hand, a larger stabilization of the first excited state would be provided by the diphenylamino group, in which the positive charge can be stabilized. Consequently, the energy gap between the ground and the first excited state would be decreased. Consistent with this interpretation is the larger Stokes shift observed for **6** (Table 1). This would enhance the intramolecular charge transfer from the donor to the acceptor to increase σ value.

The work of compounds **6** and **7** chelating with lanthanide ions is in progress.

Acknowledgments

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- Compound 5**: A mixture of CrO₃ (1 g, 1 mmol), pyridine (1.58 g, 2 mmol) and CH₂Cl₂ (100 ml) was stirred at room temperature for 20 min. A solution of **4** (0.45 g, 2 mmol) in CH₂Cl₂ (10 ml) was added dropwise over 30 min at 25–30 °C. The mixture was stirred for 5 h at room temperature. The organic phase was washed with 1 mol/L HCl, water successively and dried over MgSO₄. The crude product was purified by silica gel column chromatography eluting with petroleum/ethyl acetate to afford **5** (0.33 g), yield 75%. Mp: 186–188 °C. ¹H NMR (CDCl₃, δ ppm): 10.2 (s, 1H, CHO), 8.7 (s, 2H), 4.1 (s, 6H, OCH₃). EI-MS: *m/z* 223 (M⁺).
Compound 6: To a 50 ml two-necked flask, 0.115 g **5** (0.5 mmol), 0.323 g phosphonium salt (0.6 mmol) and 100 ml anhydrous THF were added under a nitrogen atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. A THF solution (15 ml) of 0.024 g NaH was dropped into the flask. After the reaction mixture was stirred for 24 h at room temperature, the mixture was washed with water. The organic phase was dried over MgSO₄, then evaporated to give yellow solid. The crude product was purified by chromatograph on silica gel, using CH₂Cl₂/hexane as the eluent to give pure product in 50% yield (119 mg). Mp 193–195 °C. IR (KBr) 2953.9, 2925.3, 2851.7, 1711.6, 1585.0, 1491, 1356, 1278.5, 1249.9, 1115.1, 992.5, 967.9, 759.6, 694.2 cm⁻¹. ¹H NMR

(CDCl₃, δ ppm): 8.35(s, 2H), 7.4–7.46 (m, 2H), 7.28–7.34 (m, 4H), 7.15 (d, J = 8.4 Hz, 4H), 7.03–7.13 (m, 4H), 6.95–7.0 (d, J = 16.8 Hz, 2H), 4.0 (s, 6H). EI-MS: m/z 464 (M⁺).

Compound 7: Use the same method of **6**, 45%, mp 200–202 °C. IR (KBr): 2953.9, 2921.2, 2855.8, 2802.7, 1752.5, 1711.6, 1609.5, 1589.1, 1446.1, 1258.1, 1237.7, 1184.6, 1155.9, 992.5, 955.7, 804.5 cm⁻¹. ¹H NMR (CDCl₃, δ ppm): 8.35 (s, 2H), 7.4–7.5 (m, 3H), 6.7–7.0 (m, 3H), 4.0 (s, 6H), 3.0 (s, 6H). EI-MS: m/z 340 (M⁺).
Compound 8: To a 100 ml flask, 50 mg (0.224 mmol) **5** and 30 ml anhydrous ethanol were added. After the mixture was stirred for 30 min at room temperature, 30.5 mg (0.224 mmol) *N,N*-dimethylaniline was added. The reaction mixture was refluxed for 4 h and then cooled to room temperature. The resulting precipitate was filtered and recrystallized from ethanol to give yellow crystals in 85% yield (65 mg). Mp 192–193 °C. IR (KBr): 2949.8, 2884.5,

2806.8, 1752.5, 1719.8, 1625.8, 1576.8, 1442.0, 1339.8, 1245.8, 1204.9, 1160.0, 996.6, 816.8, 780.0 cm⁻¹. ¹H NMR (CDCl₃, δ ppm): 8.8 (s, 2H), 8.6 (s, 1H), 7.4 (d, J = 8.8 Hz, 4H), 4.1 (s, 6H), 3.1 (s, 6H). EI-MS: m/z 341 (M⁺).

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