Diphenylamine end-capped 1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) derivatives with large two-photon absorption cross-sections and strong two-photon excitation red fluorescence[†]

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Novel donor- π -bridge-acceptor- π -bridge-donor (D- π -A- π -D)type 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) derivatives with end-capping diphenylamine groups have been synthesized and shown to exhibit large two-photon absorption cross-sections over a wide range of wavelengths with strong two-photon excitation red fluorescence.

Organic molecules exhibiting large two-photon absorption (TPA) cross-sections (δ) have received increasing attention owing to potential applications in three-dimensional (3-D) fluorescence imaging,¹ optical power limitation,² lasing up-conversion,³ 3-D optical data storage,⁴ 3-D microfabrication⁵ and photodynamic therapy.⁶ A variety of compounds exhibiting large δ , including donor-acceptor-donor (D-A-D)-type molecules, donor- π -bridge-acceptor (D- π -A)-type molecules, donor- π -bridge-donor (D- π -D)-type molecules, macrocycles, dendrimers, polymers and multi-branched compounds, have been synthesized and their structure-property relationships investigated.⁷ However, most of them employ C=C bonds as conjugation bridges and emit blue and green fluorescence. Although C=C bonds are effective conjugation bridges, they readily undergo trans-cis photoisomerization, photooxidation and photodegradation, which may hamper the efficiency and lifetime of materials.⁸ The drawback of C=C bonds can be avoided if one uses aromatic and heteroaromatic rings as conjugation bridges. Red emission can be realized in such molecules, with enhanced intramolecular charge transfer (ICT) and a large Stokes shift. Recently, Mataka et al. reported that $D-\pi-A-\pi-D$ -type 2,1,3-benzothiadiazole derivatives with end-capping diarylamine groups showed a maximal δ of 50–200 GM and an orange-red emission excited under laser wavelengths 600-670 nm.9 However, structurally stable TPA dyes exhibiting a large δ and also emitting strong red fluorescence via direct two-photon excitation at a longer wavelength are still scarce at present.

1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (**DPP**) and its derivatives represent a class of brilliant red and strongly fluorescent high performance pigments that have exceptional light, weather and heat stability, and a high light fastness.¹⁰



Scheme 1 Synthetic routes and structure of DPP-based two-photon dyes.

Recently, attempts have been made to use DPP-based polymers as highly luminescent,¹¹ electroactive¹² and photoactive¹³ materials in optoelectronic devices. We considered **DPP** may be a useful π -center for TPA fluorophores. However, to the best of our knowledge, there are no reports on the synthesis and TPA properties of DPP-based derivatives. In this work, we connect electron-donating diphenylamine and triphenylamine groups to the 3,6-positions of electronwithdrawing pyrrolo[3,4-c]pyrrole-1,4-dione via 1,4-phenylene conjugation bridges to form novel $D-\pi-A-\pi-D$ -type TPA dyes (DPP-DPA and DPP-TPA, Scheme 1). The results show that these DPP-based conjugated molecules exhibit large TPA cross-sections (δ_{max} = 900–1200 GM) and emit strong ($\Phi = 0.35$ –0.47) red two-photon excitation fluorescence (TPEF, $\lambda_{em} = 594-608$ nm). The δ_{max} values of these **DPP** derivatives are not only comparable with two-photon chromophores having aromatic rings as conjugation bridges reported in the literature,^{9,14} but also comparable with those of the similar sized chromophores with C=C and C=C bonds as conjugation bridges.⁷ In addition, we have found that **DPP** itself (**DPP-R**) has a comparable δ . These results demonstrate that **DPP** is a novel and efficient π -center for the construction of two-photon chromophores with strong red emissions.

To synthesize **DPP-DPA** and **DPP-TPA**, 3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (**DPP**) was firstly prepared by the reaction of diisopropyl succinate with 2 mol equiv. of 4-bromobenzonitrile in the presence of t-amyloxide sodium. Subsequently, **DPP** was converted to soluble **DPP-R**

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Fig. 1 Normalized one-photon absorption (left) and emission (right) spectra of **DPP**-based two-photon dyes in chloroform.

by eliminating the intermolecular hydrogen bonds $(N \cdots H \cdots O)$ via N-alkylation of the lactam units. Palladiumcatalyzed C–N bond formation between **DPP-R** and diphenylamine afforded **DPP-DPA**. **DPP-TPA** was by the Suzuki coupling of **DPP-R** with triphenylamine boronic acid. The structures of these **DPP**-based derivatives were unambiguously confirmed by ¹H and ¹³C NMR spectroscopy and elemental analysis (see the ESI†).

The normalized one-photon absorption and emission spectra of DPP-DPA, DPP-TPA and DPP-R in chloroform are displayed in Fig. 1. Their spectral properties are summarised in Table 1. The end-capping of DPP-R with triphenylamine and diphenylamine leads to large bathochromic shifts from 476 to 508 and 539 nm respectively. This originates from enhancement of the intramolecular charge transfer (ICT) between the terminal amino groups and the DPP core induced by the formation of the D– π –A– π –D configuration. The ICT effect of DPP-TPA is weaker (smaller red shift) than that of DPP-DPA, which indicates that the benzene ring is not an effective conjugation bridge, probably due to the non-planar biphenyl structure. As expected, DPP-TPA and DPP-DPA emit red fluorescence because of their strong ICT effects. Moreover, DPP-DPA shows a large red-shifted emission (604 nm) with a low fluorescence quantum yield ($\Phi = 0.37$) compared to **DPP-TPA** (595 nm, $\phi = 0.46$) as a result of its

stronger ICT and the decreased energy gap between the ground and Franck-Condon states.

The δ values were determined by a two-photon-induced fluorescence measurement technique using femtosecond laser pulses (160 fs, 1 kHz)¹⁵ over a relatively wide range of wavelengths, which avoids possible complications due to excited state excitation, The occurrence of non-linear absorption was confirmed by the linear dependence of the output fluorescence intensity on the square of the input laser power (Fig. S1, see the ESI†). The good overlap between one- and two-photon excitation fluorescence (Fig. 3 and Fig. S2†) indicates that the emissions occurs from the same excited state, regardless of the mode of excitation.

Fig. 2 shows that the maximal TPA cross-section (δ_{max}) of **DPP-DPA** and **DPP-TPA** are 1200 and 920 GM, respectively. These δ and δ/MW (the TPA cross-section per molecular weight) values are large and comparable to those of most chromophores having benzene, anthracene and fluorene as centers and C=C bonds as conjugation bridges (Table 1).¹⁶ The δ_{max}/MW of **DPP-DPA** and **DPP-TPA** are 2.98 and 1.68, respectively, which are valuable because molecules with $\delta_{max}/MW > 1.0$ have been found to be useful for applications that require strong TPA, such as optical limiting and 3-D microfabrication, or strong TPEF, such as bioimaging.^{7b} In addition, we found that **DPP** itself (**DPP-R**) emits a strong



Fig. 2 Two-photon spectra of DPP-based two-photon dyes measured in 2×10^{-4} M chloroform solutions.

Table 1 One- and two-photon properties of TPA dyes

Compound	$\lambda_{\rm UV}/{ m nm}^a$	$\lambda_{\mathrm{PL}}/\mathrm{nm}^b$	$\Delta u/\mathrm{cm}^{-1c}$	\varPhi^d	$\lambda_{\mathrm{TPA}}/\mathrm{nm}^{e}$	$\delta_{ ext{max}}/ ext{GM}^{f}$	$\delta_{ m max}/ m MW$
DPP-R	476	546	2650	0.67	730	110	0.31
DPP-DPA	539	604	1930	0.37	810	1200	2.98
DPP-TPA	508	595	2880	0.46	820	930	1.68
Ph-H ^g	408	455	1040	0.88	730	995	2.70
Ph-CN ^h	472	525	1700	0.86	835	1940	2.91
An-H ⁱ	455	487	1440	0.78	800	1100	2.35
An-CN ^{<i>j</i>}	587	656	1790	0.11	990	2290	4.41
$\mathbf{F} - \mathbf{H}^k$	415	457	2210	0.79	740	1260	2.60

^{*a*} The wavelength of the longest wavelength band in the one-photon absorption spectrum. ^{*b*} λ_{max} of the one-photon fluorescence spectrum. ^{*c*} Stokes shift. ^{*d*} Fluorescence quantum yield. ^{*e*} λ_{max} of the TPA spectrum. ^{*f*} The peak TPA cross-section in 10^{-50} cm⁴ s photon⁻¹ (GM). ^{*g*} 1,4-Bis(*p*-dibutylaminostyryl)benzene; the data are taken from ref. 16*a*. ^{*h*} 1,4-Bis(dibutylaminostyryl)-2,5-dicyanobenzene; the data are taken from ref. 16*a*. ^{*i*} 2,6-Bis(dihexylaminostyryl)-9,10-dicyanoanthracene; the data are taken from ref. 16*b*. ^{*k*} 2,7-Bis(dibutylaminostyryl)-9,9-dinonylfluorene; the data are taken from ref. 16*c*.



Fig. 3 Normalized one-photon absorption (OPE) and two-photon excitation (TPE) spectra (left), and one-photon (OPEF) and two-photon (TPEF) excitation fluorescence spectra (right) of **DPP-DPA**. The two-photon spectra are plotted against $\lambda/2$ (twice the photon energy).

two-photon excitation fluorescence ($\phi = 0.67$) and shows a comparable δ ($\delta_{max} = 110$ GM) value to that of rhodamine B. It was also noted that all the DPP-based chromophores studied here showed good color purity with full width half-maximums of 38-50 nm excited by both one and two photons (Fig. 1 and Fig. S2). Fig. 3 shows that the two-photon allowed state (twice the photon energy) of DPP-DPA is located at a shorter wavelength than the ICT absorption band (the longest wavelength region), as predicted by symmetry.¹⁷ It can be seen that the maximal two-photon excitation wavelength of **DPP-DPA** is close to that of the absorption maxima. The TPA cross-section would increase if the two-photon allowed states were close to the Franck-Condon state.¹⁸ A similar result was observed for all the **DPP**-based chromophores (Fig. S2[†]).

In conclusion, we have synthesized novel $D-\pi-A-\pi-D$ -type 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) derivatives with stable chemical structures and measured their TPA properties using femtosecond laser pulses. They exhibit large δ values and emit strong red fluorescence in a TPA process that can be attributed to enhanced ICT between the amino groups and the DPP core. DPP itself also shows a valuable δ value. This work, for the first time, provides a novel and efficient π -center for the construction of two-photon chromophores with stable structures, strong red emissions and large δ values.

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