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Solvatofluorochromic, non-centrosymmetric π -expanded diketopyrrolopyrrole†

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A novel non-centrosymmetric π -expanded diketopyrrolopyrrole was designed and synthesized. Strategic placement of *tert*-butyl groups at the periphery of a diketopyrrolopyrrole allowed us to selectively fuse one moiety *via* tandem Friedel–Crafts–dehydration reactions, resulting in a non-centrosymmetric dye. The structure of the dye was confirmed by X-ray crystallography, revealing that it contains a nearly flat arrangement of four fused rings. Extensive photophysical studies of this new functional dye revealed that the intensity of its emission strongly depends on solvent polarity, which is typical for dipolar chromophores. In non-polar solvents, the fluorescence quantum yield is high whereas in polar solvents such as MeOH, it is 12%. However, upon two-photon excitation the compound behaves like a centrosymmetric dye, showing a two-photon absorption maximum at significantly shorter wavelengths than twice the wavelength of the one-photon absorption maximum.

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Introduction

Current methods for fluorescence imaging rely on classical dyes such as fluorescein, rhodamines and coumarins.¹ The advent of new luminescent probes is growing in the literature ranging from organic chromophores,¹ quantum dots,² carbon dots,³ organic nanodots,⁴ fluorescent organic nanoparticles,⁵ *etc.* Notwithstanding new options, it is clear that organic chromophores, due to their tunability and possibility to attach to sensing units, continue to prevail in real-world applications.⁶ Among various targets, non-centrosymmetric π -conjugated systems, whose fluorescence is dependent on solvent polarity, are one of the most important tributes.⁷ The subtle interplay between centrosymmetric and non-centrosymmetric structures has been recently revealed by a few breakthrough approaches showing that (a) quadrupolar molecules can display solvato-

fluorochromism due to symmetry breaking in the excited-state⁸ and (b) the emission properties of dipolar fluorophores in aqueous media can be significantly altered by replacing the donor amino substituent with a very polar one.⁹

Application of diketopyrrolopyrroles (DPPs, 1,4-diketo-2*H*,5*H*-pyrrolo[4,3-*c*]pyrroles) began as red-pigments of unprecedented light-fastness.¹⁰ In recent decades however, applications of DPPs have been reinvented as they have found new uses in diverse areas of applications such as optoelectronics and molecular electronics. DPPs' derivatives have been widely employed in fields such as dye-sensitized solar cells,¹¹ light emitting diodes,¹² organic field effect transistors¹³ and above-all, bulk-heterojunction solar cells.^{14,15} Certain attention has also been focused on its inversed analogue – pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (iDPP).¹⁶ Although replacing phenyl substituents¹⁷ with five-membered heterocycles and their π -expanded analogues offers some opportunities in modulating the absorption and emission properties,^{11c,18} the most significant change in optical properties has been achieved by expanding the DPP-core *via* fusion with other aromatics/dyes. Four strategies towards making such compounds have been recently revealed respectively by Zumbusch,¹⁹ Shimizu,^{20a,c} Würthner^{20b} and the Gryko group.²¹ Two-photon absorbing properties of DPPs have rarely been studied despite the fact that their electron-poor core seems to be an excellent starting point for the construction of D–A–D or A–D architectures, important for generating large two-photon absorption cross-sections.^{18e,f,21b,22} Herein we would like to present a strategy towards non-centrosymmetric π -expanded diketopyrrolopyrroles.

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†Electronic supplementary information (ESI) available: Full synthetic and analytical data of compounds **2** and **3** as well as copies of ¹H NMR and ¹³C NMR spectra. CCDC 1441247. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob02583d



Design and synthesis

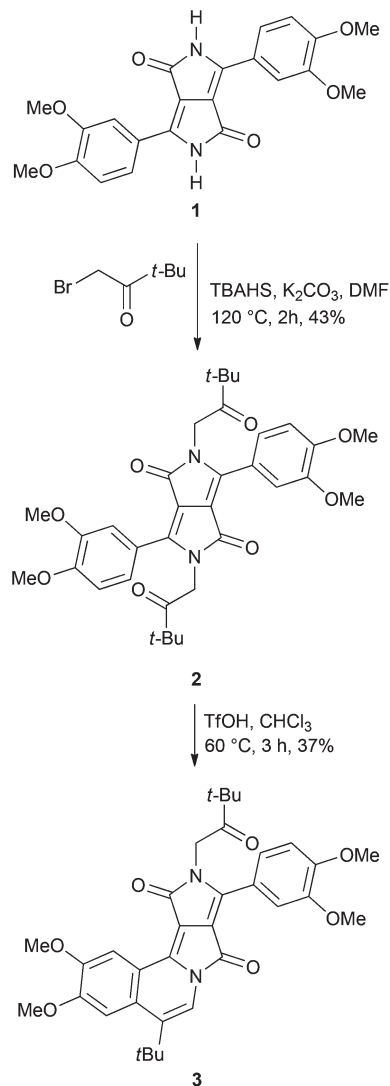
The C_2 -symmetry of diketopyrrolopyrroles and their *N*-alkylated derivatives makes it difficult to design analogous dyes lacking this symmetry. Our recently reported two-step route of the DPP chromophore expansion is not exceptional in this regard.²¹ Double alkylation of DPP pigments with 2-bromoacetaldehyde diethyl acetal and the subsequent treatment of the intermediate diacetals with acid always led to the centrosymmetric double-cyclized products. This was also the case when ketones – phenacyl bromides – were used as alkylating agents.^{21b} Mixed-alkylation of DPP with 2-bromoacetaldehyde diethyl acetal and *n*-alkyl bromide is one of the several possible strategies to synthesize non-symmetric analogues,²³ however, due to different reactivities of the two alkylating agents, the desired non-symmetrically substituted product may be obtained in low yields. Our strategy towards D–A type π -expanded diketopyrrolopyrroles is based on the use of mild conditions in the final ring-closure step. We expected that after the alkylation of DPP **1** with 1-bromo-3,3-dimethylbutan-2-one, instead of previously used bromoacetaldehyde acetal or phenacyl bromides,²¹ diketone **2** would be obtained (Scheme 1). We have decided to use 1-bromo-3,3-dimethylbutan-2-one in order to ensure that the final donor–acceptor dye would possess the moderately reactive *t*-BuCO group rather than the chemically unstable CHO functionality.

Pigment **1**, possessing electron-rich 3,4-dimethoxyphenyl substituents, was prepared according to the literature procedure^{21a} via the condensation of diisopropyl succinate with 3,4-dimethoxybenzotrile in the presence of sodium *tert*-amylate (Scheme 1). The alkylation reaction of DPP **1** with commercially available 1-bromo-3,3-dimethylbutan-2-one was performed under similar conditions as developed for the alkylation with 2-bromoacetaldehyde diethyl acetal: at 120 °C in DMF, using potassium carbonate as a base and tetrabutylammonium bisulfate (TBAHS) as a phase-transfer catalyst (Scheme 1).²¹ As previously noted,^{21b} in contrast to bromoacetaldehyde acetal, bromoketones react much faster and the reaction is finished within 2 hours (acetal required at least 16 h).

Diketone **2** was obtained in moderate yield (43%, Scheme 1). It was well soluble in chlorinated and aromatic solvents and strongly fluorescent in solutions. It is noteworthy that product **2** also exhibited intense fluorescence in the solid-state under UV irradiation.

Dye **2** was added to the reaction with triflic acid (TfOH) at 60 °C in chloroform and the progress was controlled using TLC. When the conversion of the starting material was complete (about 3 h), the main product was purified by silica gel chromatography. NMR spectra revealed that non-centrosymmetric dye **3** was formed exclusively (Scheme 1).

X-ray quality crystals have been obtained for dye **3**. Crystallographic analysis fully confirmed the structure (Fig. 1). The four-fused ring system is almost planar (deviations from the calculated plane less than 0.1 Å). Hence the presence of short hydrogen bonding between carbonyl oxygen and the benzene



Scheme 1 Synthesis of dye **3**.

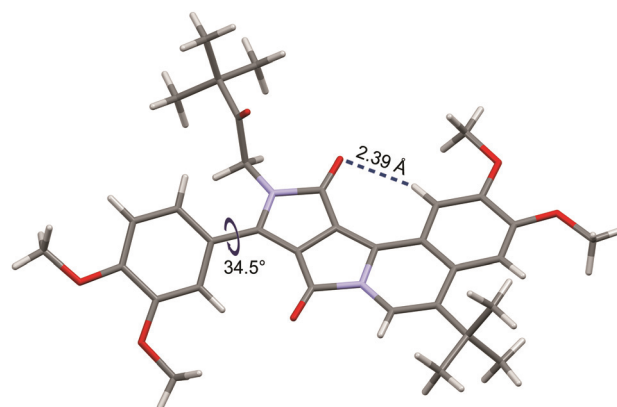


Fig. 1 The crystal structure of compound **3** (CCDC 1441247).



hydrogen atom (distance: 2.39 Å, Fig. 1) does not cause a significant deformation of the polycyclic system, as was also observed in the case of a bis-fused DPP derivative (O...H distance 2.45 Å, highest deviations from planarity: 0.34 Å).^{21b} The plane of the benzene ring in the 3,4-dimethoxyphenyl substituent is twisted by 34.5° relative to the polycyclic system. This torsion angle is similar to the corresponding angles in non-fused *N,N*-dialkyl DPPs.²⁴ In the tetragonal crystal lattice, molecules of **3** form dimers through π - π interactions, see Fig. S1.† The distance between the chromophores (3.73 Å) is noticeably longer than in the case of the bis-cyclized DPP derivative (3.48 Å),^{21b} which is due to the presence of the bulky *tert*-butyl groups.

Optical properties

The maxima of absorption (λ_{abs}) and emission (λ_{em}) for **2** are similar to those reported for previously described DPPs having 3,4-dimethoxyphenyl at 3 and 6 positions and 2,2-diethoxyethyl substituents at the nitrogen atoms,²¹ which indicates negligible perturbation by the nature of the *N*-substituents (Table 1). In chloroform, mono-fused DPP **3** has an absorption ~590 nm and an emission at ~620 nm, which results in a Stokes shift of about 800 cm⁻¹ (Fig. 2, Table 1). The absorption maximum of compound **3** is only 6 nm hypsochromically shifted *versus* its double-fused analogue **4** (Fig. 3, 587 nm *vs.* 593 nm),^{21a} whereas emission is even bathochromically shifted (619 nm *vs.* 597 nm). The Stokes shift, which in the case of centrosymmetric and rigid π -expanded DPPs is typically very small (90–230 cm⁻¹),^{21a,b} increases for compound **3** in CHCl₃ to 880 cm⁻¹ (see Table 1). These results are associated with the fact that the rigid and centrosymmetric chromophore in **4** is replaced by the more flexible, non-symmetric, push-pull system of compound **3**. The molar absorption coefficient of **3** is 27 000, only slightly higher than that before cyclization (compound **2**), but significantly lower than that of the bis-cyclized compound **4** (110 000 M⁻¹ cm⁻¹).^{21a,b}

Absorption and emission (fluorescence) spectra of compound **3** in *n*-hexane are presented in Fig. S2.† The Stokes shift

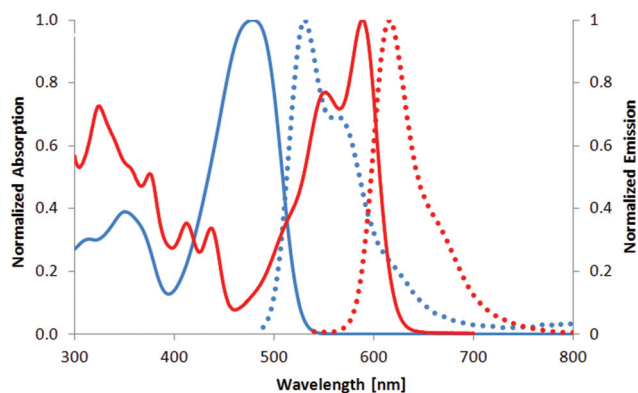


Fig. 2 Absorption (solid) and emission (dotted) spectra of compounds **2** (blue line) and **3** (red line) measured in chloroform.

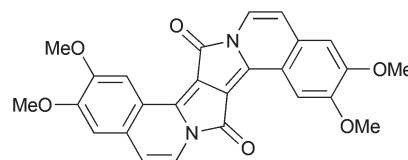


Fig. 3 The chemical structure of compound **4**.

in this solvent is relatively small, ~450 cm⁻¹. Freezing of the matrix to 5 K does not lead to noticeable sharpening of the fluorescence spectrum. The fluorescence quantum yield of **3** in *n*-hexane is 0.56, whereas the decay time of this emission is 8.37 ns (see the ESI†).

Whereas absorption does not undergo notable changes from non-polar solvents to MeCN and MeOH, the emission quantum yield drastically decreases from 0.66–0.82 in hydrocarbon solvents to 0.12 in MeOH (Table 1). Simultaneously, the emission maximum is slightly bathochromically shifted by 14 nm, when moving from non-polar pentane to polar methanol. The slight red-shift of emission seems to be related more to inhomogeneous broadening with the loss of a fine structure in more polar solvents (starting from CHCl₃). The slight red-shift cannot explain the decrease in quantum yield as it does for a push-pull system (only 4 nm from toluene to methanol).

Two-photon absorption (2PA) measurements of both of the new compounds **2** and **3** were performed using the two-photon excited fluorescence (TPEF) method (see the ESI†). Non-fused **2** possesses a moderate 2PA cross-section located around 700 nm (Table 2) resulting most probably from its quadrupolar structure. Interestingly, the new π -expanded DPP **3** possessing a dimethoxyphenyl unit has a larger maximum 2PA cross-section than centrosymmetric compound **4** studied previously (Table 2).^{20b}

Its 2PA response is also slightly higher than that of the centrosymmetric derivative **2** and does not show a clear maximum. In addition, the 2PA maximum (≤ 740 nm) of **3** is located at much shorter wavelengths than the doubled wavelength of the one-photon absorption maximum (1176 nm, see

Table 1 Spectroscopic data for dyes **2**–**4**

Compound	Solvent	$\lambda_{\text{abs}}^{\text{max}}$ [nm]	$\lambda_{\text{em}}^{\text{max}}$ [nm]	Stokes shift [cm ⁻¹]	Φ_{fl}
2	CHCl ₃	478	531	2100	0.86 ^a
3	Pentane	544, 584	605, 655	600	0.66 ^b
3	Cyclohexane	544, 585	605, 657	570	0.82 ^b
3	Toluene	550, 589	615, 655	720	0.72 ^b
3	CHCl ₃	587	619	880	0.43 ^b
3	MeCN	545, 580	619	1090	0.39 ^b
3	MeOH	543, 579	619	1120	0.12 ^b
4	CHCl ₃ ^c	593	597	110	0.85
4	DMF ^c	593	602	250	0.70

^a Standard: rhodamine 6G in EtOH ($\Phi = 0.94$). ^b Standard: cresyl violet in methanol ($\Phi = 0.54$). ^c Ref. 21a.



Table 2 Two-photon absorption data

Compound	$2\lambda_{1PA}^{\max}$ [nm]	λ_{2PA}^{\max} [nm]	$\sigma_2^{\max a}$ [GM]	$\sigma_2^{\max} \phi_{fl}$ [GM]
2	974, 708	720	260	220
3	1176, 1102, 874	≤ 740	≥ 270	≥ 120
4	1186	820	130	110

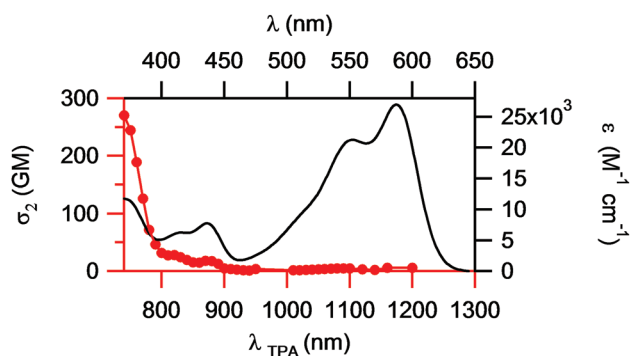
Fig. 4 One-photon absorption (solid black line) and two-photon absorption (red line) spectra of compound 3 in CHCl_3 .

Fig. 4). This is an interesting and unusual result, because such an effect is typically observed for centrosymmetric chromophores, for which one-photon allowed excitations are two-photon forbidden and *vice versa*, whereas for non-symmetric dyes both processes obey the same quantum selection rules and 2PA is usually recorded at approximately twice the wavelength of the 1PA maximum. Therefore, under the two-photon excitation, non-symmetric compound 3 behaves more like a centrosymmetric chromophore.

Calculations

Calculated excitation energies, oscillator strengths and 2PA cross-sections are listed in Table 3. We note that the strongest oscillator strength in 1PA is found for the S_1 state, and this

Table 3 Results of calculations of two-photon absorption for compound 3

Excited state	2PA energy (eV)	2PA energy (nm)	2PA cross-section (GM)	1PA oscillator strength
1	2.51	988.7	1.87	0.4151
2	3.32	747.5	42.1	0.1242
3	3.87	641.2	234.0	0.1759
4	4.17	595.1	8.9	0.1304
5	4.22	588.0	1020	0.0024
6	4.35	570.4	479	0.0454
7	4.41	562.7	252	0.0727
8	4.49	552.7	40	0.0017
9	4.56	544.2	228	0.0328
10	4.64	534.8	357	0.2408

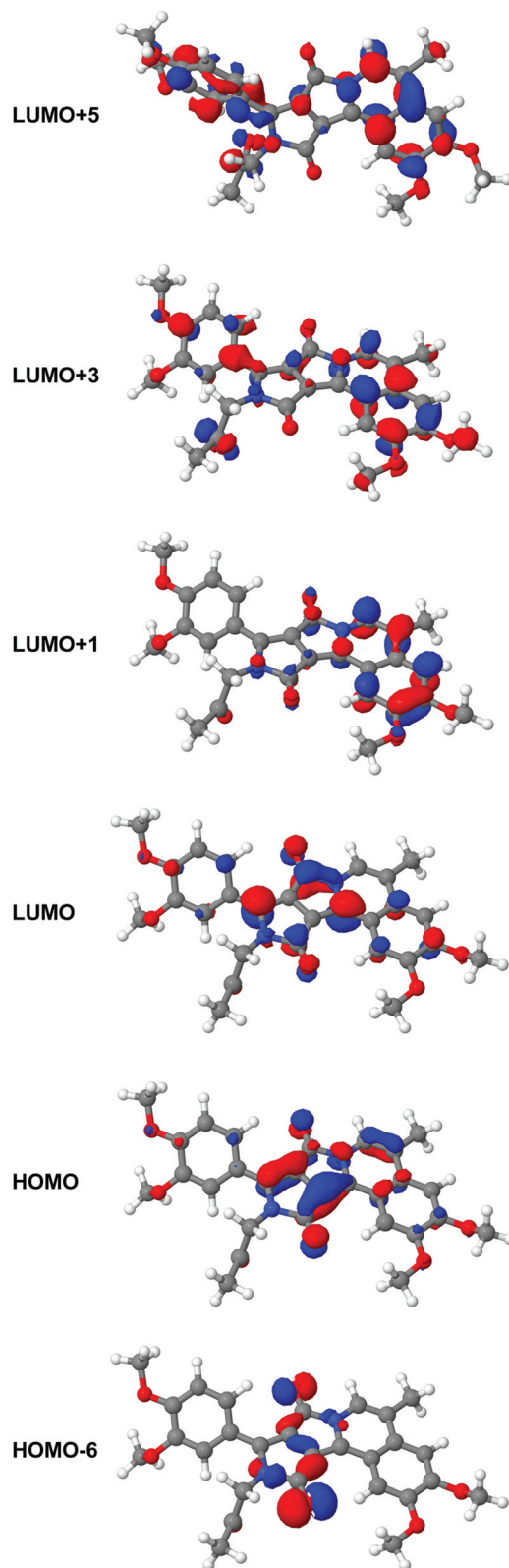


Fig. 5 From the top to bottom: LUMO+5, LUMO+3, LUMO+1, LUMO, HOMO and HOMO-6 of 3. The orbital plots have been generated from a CAM-B3LYP calculation using the aug-cc-pVDZ basis set.



transition is almost dark in 2PA. In contrast to this, the S_5 state exhibits a large 2PA cross-section. At the same time, this state is dark in 1PA. However, for the other states we do not find such a strong alternation between one- and two-photon absorption. Indeed the S_2 state shows weak activity in both processes, *i.e.*, 1PA and 2PA whereas the S_3 state shows reasonable 1PA and 2PA activities, in good agreement with the experimental data (Fig. 4). Evaluating the orbital transitions involved in the excitation to the S_1 state, we note that this state is dominated by the HOMO–LUMO transition. Both the HOMO and the LUMO are located mainly on the DPP backbone (see Fig. 5).

These parts of the HOMO are gerade with respect to the inversion center of the backbone while the corresponding contributions to the LUMO are ungerade. Hence the orbitals show pseudo-centrosymmetry explaining the strong 1PA and weak 2PA character of the states. In contrast to the S_1 state, higher electronic states S_i (in particular S_3 and S_5) involve different molecular orbital transitions. Fig. 5 shows the molecular orbitals involved in the S_1 , S_3 and S_5 states. While the S_3 state is dominated by the HOMO > LUMO+1 transition, the S_5 state involves the HOMO–6 > LUMO, HOMO > LUMO+5 and HOMO > LUMO+3-transitions. By evaluating the shape of the orbitals, we note that the HOMO–6 and the HOMO are tendentially gerade with regard to the inversion center of the DPP-backbone (as **3** is not a centrosymmetric molecule, the orbitals cannot be gerade or ungerade in the whole molecule but parts of them can show a local pseudosymmetric behavior). Also the LUMO+3 and the LUMO+5 are pseudo-gerade while the LUMO is pseudo-ungerade. The LUMO+1 cannot be classified as either gerade or ungerade as it is mostly located on the isoquinoline moiety. This explains why the S_3 state shows both 1PA and 2PA activities while the S_1 state is only active in 1PA and the S_5 state only in 2PA. Both states have charge-transfer character. The result of such transitions is to change the dipole moment of a molecule in the excited state, and it promotes a greater cross-section for two-photon transitions.²⁵

Conclusions

In summary, we have proven that cascade processes leading to π -expanded diketopyrrolopyrroles can be controlled to lead to a donor–acceptor type product. The resulting heterocycle possesses four conjugated rings and lacks a center of symmetry. However, 1PA and 2PA measurements revealed that the final dye simultaneously exhibits photophysical characteristics of both symmetric and non-symmetric chromophores. This behavior is in agreement with the results of DFT calculations, and can be explained by analysis of the symmetry of the molecular orbitals in this molecule. This provides a synthetic entry to bright, red-emitting two-photon fluorophores. The other notable finding is that breaking the overall symmetry of a molecule does not necessarily extinguish the symmetry completely. Some molecular properties and excited states still can show “pseudosymmetric behavior”. This study is complemen-

tary to the investigation of solvatochromism for centrosymmetric bis(thienyl)DPPs^{18d} and at the same time it offers opportunities in fluorescence imaging.

Experimental section

General

All chemicals were used as received unless otherwise noted. All reported ¹H NMR and ¹³C NMR spectra were recorded on a 200, 400, 500 or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; J values are given in Hz. UV-Vis and fluorescence spectra were recorded in chloroform. Chromatography was performed on silica (Kieselgel 60, 200–400 mesh). 1,4-Diketo-3,6-bis(3,4-dimethoxyphenyl)pyrrolo[3,4-*c*]pyrrole (**1**)^{21a} was prepared according to the literature procedures.

3,6-Bis(3,4-dimethoxyphenyl)-2,5-bis(3,3-dimethyl-2-oxobutyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole (2). A mixture of pigment **1** (408 mg, 1.0 mmol), tetrabutylammonium bisulfate (TBAHS, 17 mg, 0.05 mmol), potassium carbonate (2.07 g, 15 mmol) and 25 ml of DMF was heated to 120 °C under an argon atmosphere. 1-Bromo-3,3-dimethylbutan-2-one (0.67 ml, 5.0 mmol) was then added dropwise by using a syringe (about 30 min). The reaction mixture was stirred for an additional 1.5 h, cooled and diluted with water and dichloromethane. The aqueous layer was extracted with dichloromethane, the combined organic layers were washed with water and brine and dried over sodium sulfate. Solvents were evaporated, the product was separated by column chromatography (silica, dichloromethane : acetone 49 : 1 \rightarrow 19 : 1). Finally, the product was recrystallized by slow addition of pentane to the solution of the product in a small amount of CHCl₃. Yield: 258 mg (43%). Red powder. Mp 203–204 °C (CHCl₃/pentane). ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 2.0 Hz, 2H, 2-H at Ar), 7.19 (dd, J = 8.5, 2.0 Hz, 2H, 6-H at Ar), 6.91 (d, J = 8.5 Hz, 2H, 5-H at Ar), 4.75 (s, 4H, CH₂), 3.92 (s, 6H, OCH₃), 3.91 (s, 6H, OCH₃), 1.19 (s, 18H, *t*Bu). ¹³C NMR (126 MHz, CDCl₃) δ 209.3, 162.5, 151.5, 149.2, 148.1, 121.8, 120.7, 112.0, 111.0, 109.2, 56.2, 56.0, 47.1, 43.4, 26.4. HRMS (ESI) calcd for C₃₄H₄₀N₂O₈Na (M + Na⁺): 627.2682, found: 627.2678.

5-*tert*-Butyl-9-(3,4-dimethoxyphenyl)-10-(3,3-dimethyl-2-oxobutyl)-2,3-dimethoxy-8H-pyrrolo[3',4':3,4]pyrrolo[2,1-*a*]isoquinoline-8,11(10H)-dione (3). Diketone **2** (151 mg, 0.25 mmol) was dissolved in 5 ml of dry chloroform under an argon atmosphere. Subsequently trifluoromethanesulfonic acid (0.49 ml, 5.5 mmol) was slowly added and the reaction mixture was stirred at 60 °C for 3 h. The resulting mixture was then diluted with water and dichloromethane and was separated. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water and dried over sodium sulfate. The product was purified by column chromatography (dichloromethane) and recrystallized by slow addition of pentane to the solution of the product in a small amount of CHCl₃. **3** (54 mg, 37%) was obtained as a dark brown solid. Mp 275–277 °C (CHCl₃/pentane). ¹H NMR



(500 MHz, CDCl₃) δ 8.81 (s, 1H, Ar-H), 7.59 (s, 1H, Ar-H), 7.50 (d, J = 2.0 Hz, 1H, 2-H at 3,4-dimethoxyphenyl), 7.47 (s, 1H, Ar-H), 7.08 (dd, J = 8.5, 2.0 Hz, 1H, 6-H at 3,4-dimethoxyphenyl), 6.90 (d, J = 8.5 Hz, 1H, 5-H at 3,4-dimethoxyphenyl), 4.87 (s, 2H, CH₂), 4.13 (s, 3H, OCH₃), 4.03 (s, 3H, OCH₃), 3.97 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 1.53 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu). ¹³C NMR (126 MHz, CDCl₃) δ 209.3, 160.8, 157.9, 152.6, 151.2, 149.2, 149.0, 147.2, 141.1, 129.9, 128.9, 121.2, 120.7, 119.8, 117.7, 112.2, 110.8 (2 signals), 108.7, 107.8, 98.3, 56.5, 56.2, 56.0 (2 signals), 47.4, 43.4, 34.3, 30.8, 26.5. HRMS (EI 70 eV) calcd for C₃₄H₃₈N₂O₇ (M⁺): 586.2679, found: 586.2682.

Optical studies

One-photon absorption spectra were measured with a Perkin Elmer Lambda 35 UV/VIS spectrometer. Fluorescence spectra at room and at 5 K were measured with the aid of a home-built set-up equipped with a liquid helium optical cryostat, a McPherson 207 monochromator, an EMI 9659 photomultiplier and an electronic card inserted into a PC. The excitation source was a Coherent Verdi-V5 (532 nm) and a Coherent 700 dye laser (with the simplified optics for a cw operation at 568.5 nm).

Fluorescence decay curves were monitored with the aid of a "time correlated" single photon counting technique (in inverted time mode). The system composed of a mode-locked Coherent Mira-HP laser pumped by a Verdi 18 laser, an APE Pulse selector reducing the repetition of Mira laser pulses to 2 MHz, and a frequency doubling crystal. Fluorescence photons, dispersed with a McPherson 207 monochromator, were detected with a HMP-100-50 hybrid detector and a SPC-150 module inserted into a PC, both from Becker&Hickl GmbH.

Two-photon absorption cross-sections of 10⁻⁴ M solutions were measured relative to fluorescein in 0.01 M aqueous NaOH for 700–800 nm,²⁶ using the well-established method described by Xu and Webb^{26b} and the appropriate solvent-related refractive index corrections.²⁷ The reference values between 700 and 715 nm for fluorescein were taken from the literature.²⁸ The quadratic dependence of the fluorescence intensity on the excitation power was checked for each sample and all wavelengths. To span the 700–980 nm range, a Nd:YLF-pumped S2 Ti:sapphire oscillator was used generating 150 fs pulses at a 76 MHz rate. To span the 1000–1400 nm range, an OPO (PP-BBO) was added to the setup to collect and modulate the output signal of the Ti:sapphire oscillator.

Computational studies

To simplify the computational treatment, the two *t*-butyl groups in molecule **3** have been replaced by methyl groups. The *t*-butyl groups are not expected to influence the absorption properties of the molecule, but to increase the computational complexity because of the increases in the number of atoms and increases in the conformational freedom. The modified structure will be referred to as molecule **3a**. The structure of **3a** has been optimized using the B3LYP density functional²⁹ and

the TZVP basis set³⁰ using the TURBOMOLE suite of programs.³¹ Two-photon absorption calculations have been carried out using DALTON³² using the CAM-BL3LYP density functional³³ and the aug-cc-pVDZ basis set from the Dunning family of basis sets.³⁴

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