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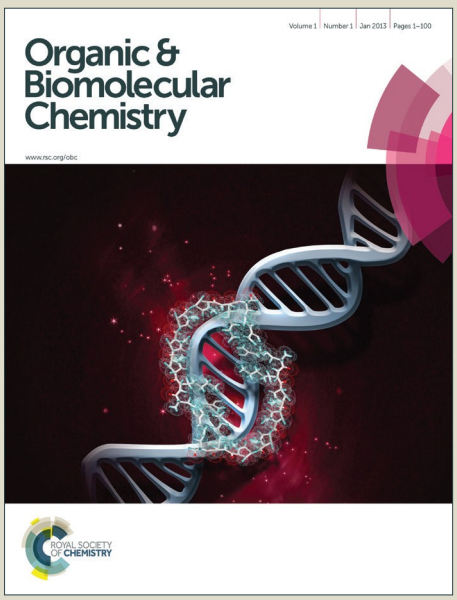

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ARTICLE TYPE

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 diketopyrrolopyrrole allowed us to selectively fuse one moiety *via* tandem Friedel-Crafts-dehydratation 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 intensity of its emission strongly depends on the 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.

Introduction

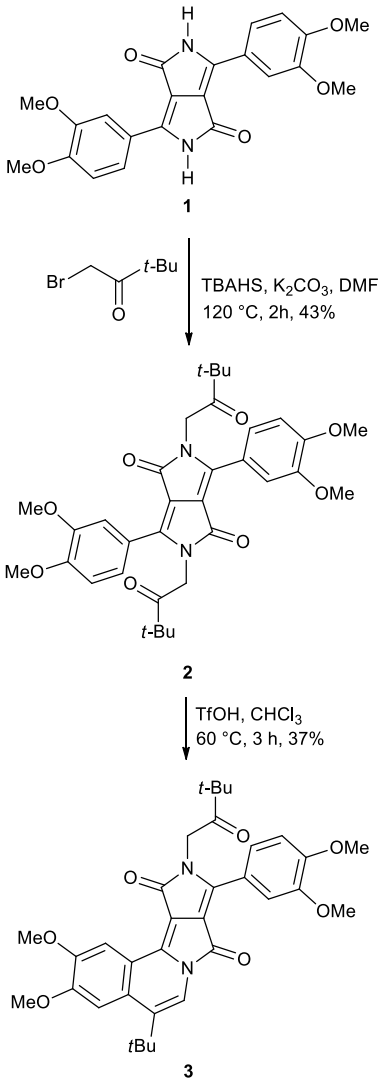
Current methods for fluorescence imaging rely on classical dyes such as fluorescein, rhodamines and coumarins.[1] The advent of new luminescent probes is growing in literature ranging from organic chromophores,[1] quantum dots,[2] carbon dots,[3] organic nanodots,[4] fluorescent organic nanoparticles,[5] 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 solvatofluorochromism due to symmetry breaking in the excited-state[8] and b) emission properties of dipolar fluorophores in aqueous media can be significantly altered by replacing the donor amino substituent with 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 a 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 transistors[13] 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 substituents[17] 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 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.

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 several possible strategies to synthesize non-symmetric analogues,[23] however, due to different reactivity 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 will possess the moderately reactive *t*-BuCO group rather than chemically unstable CHO functionality.



Scheme 1 Synthesis of dye **3**.

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-dimethoxybenzonitrile 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 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 exhibit 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).

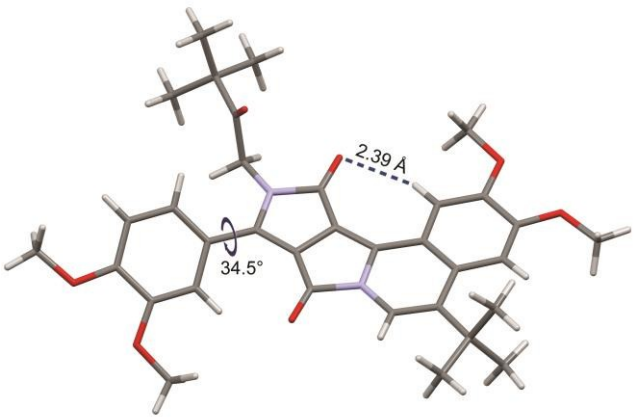


Figure 1 The crystal structure of compound **3** (CCDC 1441247).

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 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 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 Figure 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 DPP 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 maxima 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 case of centrosymmetric and rigid π-expanded DPPs is typically very small (90–230 cm^{-1}),[21a,b] increases for compound **3** in $CHCl_3$ 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 27000, only slightly higher than before cyclization (compound **2**), but significantly lower than for the bis-cyclized compound **4** (110000 M^{-1} cm^{-1}).[21a,b]

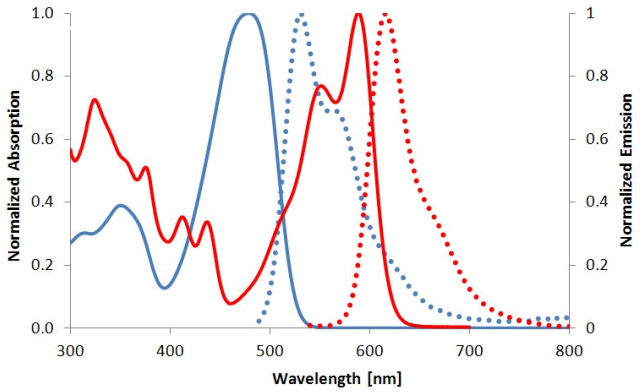


Fig. 2 Absorption (solid) and emission (dotted) spectra of compounds **2** (blue line) and **3** (red line) measured in chloroform.

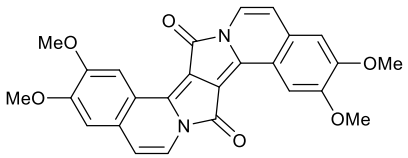


Figure 3 The chemical structure of compound **4**.

Absorption and emission (fluorescence) spectra of compound **3** in *n*-hexane are presented in Fig. S2. The Stokes shift 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. Fluorescence quantum yield of **3** in *n*-hexane is 0.56, whereas the decay time of this emission is 8.37 ns (see ESI).

Whereas absorption does not undergo notable changes from non-polar solvents to MeCN and MeOH, 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 going from non-polar pentane to polar methanol. The slight red-shift of emission seems to be related more to inhomogeneous broadening with loss of fine structure in more polar solvent (starting from $CHCl_3$). 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).

Table 1 Spectroscopic data for dyes **2**-**4**.

Compound	solvent	λ_{abs}^{max} [nm]	λ_{em}^{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 (Φ = 0.94); [b] Standard : cresyl violet in methanol (Φ = 0.54); [c] Ref. 21a.

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 ESI). Non-fused **2** possesses 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]

Table 2 Two-photon absorption data

Compound	$2\lambda_{1PA}^{max}$ [nm]	λ_{2PA}^{max} [nm]	σ_2^{max} [GM][a]	$\sigma_2^{max}\Phi_{fl}$ [GM]
2	974, 708	720	260	220
3	1176, 1102, 874	≤ 740	≥ 270	≥ 120
4	1186	820	130	110

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 Figure 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.

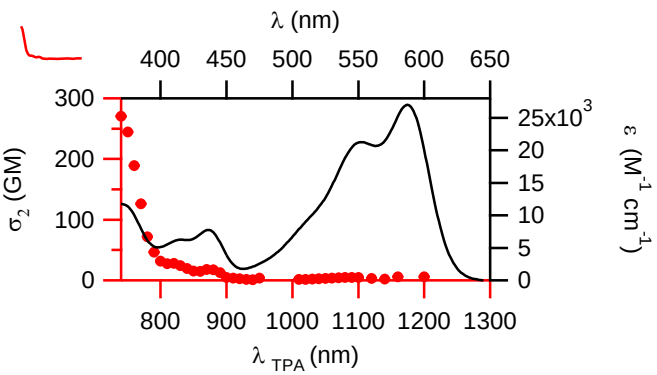


Fig. 4 One-photon absorption (solid black line) and two-photon absorption (red line) spectra of compound **3** in $CHCl_3$.

Calculations

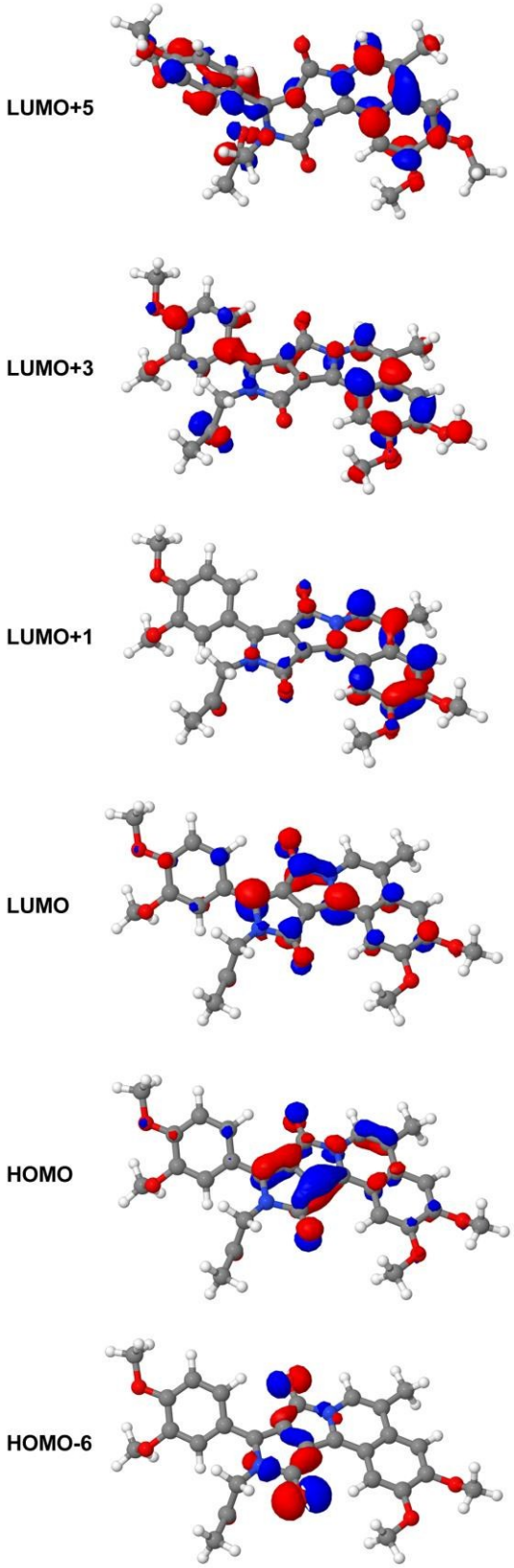


Fig. 5 From the top to bottom: LUMO+5, LUMO+3, LUMO+1, LUMO, HOMO and HOMO-6 of **3**. The orbital plots have been generated from a CAM-B3LYP calculation using the aug-cc-pVDZ basis set.

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 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 activity, in good agreement with experimental data (Figure 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 Figure 5).

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

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. Figure 5 shows the molecular orbitals involved in the S1, S3 and S5 states. While the S3 state is dominated by the HOMO > LUMO+1 transition, the S5 state involves the HOMO-6 > LUMO, HOMO > LUMO+5 and HOMO > LUMO+3-transitions. 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 S3 state shows both 1PA and 2PA activity while the S1 state is only active in 1PA and the S5 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 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 exhibit 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 symmetry completely. Some molecular properties and excited states still can show "pseudosymmetric behavior". This study is complementary to investigation of solvatofluorochromism for centrosymmetric bis(thienyl)DPPs[18d] and at the same time it offers opportunities in fluorescent imaging.

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Experimental Section

General: All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on 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 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, combined organic layers were washed with water and brine and dried over sodium sulfate. Solvents were evaporated, the product was separated by the column chromatography (silica, dichloromethane : acetone 49 : 1 → 19 : 1). Finally the product was recrystallized by slow addition of pentane to the solution of product in small amount of $CHCl_3$. Yield: 258 mg (43%). Red powder. Mp 203-204 °C ($CHCl_3$/pentane). ^{1}H NMR (500 MHz, $CDCl_3$) 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, CH_2), 3.92 (s, 6H, OCH_3), 3.91 (s, 6H, OCH_3), 1.19 (s, 18H, *t*Bu). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{34}H_{40}N_2O_8Na$ ($M+Na^+$): 627.2682, found: 627.2678.

5-*tert*-Butyl-9-(3,4-dimethoxyphenyl)-10-(3,3-dimethyl-2-oxobutyl)-2,3-dimethoxy-8*H*-pyrrolo[3',4':3,4]pyrrolo[2,1-*a*]isoquinoline-8,11(10*H*)-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 were 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 the column chromatography (dichloromethane) and recrystallized by slow addition of pentane to the solution of product in small amount of $CHCl_3$. **3** (54 mg, 37%) was obtained as a dark brown solid. Mp 275-277 °C ($CHCl_3$/pentane). ^{1}H NMR (500 MHz, $CDCl_3$) 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, CH_2), 4.13 (s, 3H, OCH_3), 4.03 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 1.53 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu). ^{13}C NMR (126 MHz, $CDCl_3$) 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 70eV) calcd for $C_{34}H_{38}N_2O_7$ (M^+): 586.2679, found: 586.2682.

Optical studies:

One-photon absorption spectra were measured with 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, McPherson 207 monochromator, EMI 9659 photomultiplier and electronic card inserted into a PC. 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 "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 repetition of a 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] Reference values between 700 and 715 nm for

fluorescein were taken from 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 the molecule **3** have been replaced by methyl groups. The *t*-butyl groups are not expected to influence the absorption properties of the molecule, but increases the computational complexity because of the increases in the number of atoms and increases the conformational freedom. The modified structure will be referred to as molecule **3a**. The structure of **3a** has been optimized using the B3LYP density functional[29] and the TZVP basis set[30] using the TURBOMOLE suite of programs.[31] Two-photon absorption calculations have been carried out using DALTON[32] using the CAM-BL3LYP density functional[33] and the aug-cc-pVDZ basis set from the Dunning family of basis sets.[34]

Notes and references

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† Electronic Supplementary Information (ESI) available: [full synthetic and analytical data of compounds **2** and **3** as well as copies of ^{1}H NMR and ^{1}C NMR spectra]. See DOI: 10.1039/b000000x/

1 (a) R. Y. Chao, M.-F. Ding, J.-Y. Chen, C.-C. Lee, S.-T. Lin and J. Chin., *Chem. Soc*., 2010, **57**, 213-221; (b) I. Kim, D. Kim, S. Sambasivan,and K. H. Ahn, *Asian J. Org. Chem*., 2012, **1**, 60-64; (c) J. Avó, S. Martins, A. J. Parola, J. C. Lima, P. S. Branco, J. P. Prates Ramalho, and A. Pereira, *ChemPlusChem*, 2013, **78**, 789-792; (d) T. Mineno, T. Ueno, Y. Urano, H. Kojima,and T. Nagano, *Org. Lett*., 2006, **8**, 5963-5966; (e) T. Hirano, K. Kikuchi, Y. Urano, T. Higuchi, and T. Nagano, *J. Am. Chem. Soc*., 2000, **122**, 12399-12400; (f) N. Boens, V. Leen, and W. Dehaen, *Chem. Soc. Rev*., 2012, **41**, 1130-1172; (g) G. Ulrich, R. Ziessel,and A. Harriman, *Angew. Chem., Int. Ed*., 2008, **47**, 1184-1201; (h) T. A. Wood and A. Thompson, *Chem. Rev*., 2007, **107**, 1831-1861.

2 (a) O. S. Wolfbeis, *Chem. Soc. Rev*., 2015, **44**, 4743-4768; (b) Z. Li, Q. Sun, Y. Z., B. Tan, Z. P. Xu and S. X. Dou, *J. Mater. Chem. B*, 2014, **2**, 2793-2818; (c) K. D. Wegner and N. Hildebrandt, *Chem. Soc. Rev*., 2015, **44**, 4792-4834.

3 (a) P. G. Luo, F. Yang, S.-T. Yang, S. K. Sonkar, L. Yang, J. J. Broglie, Y. Liu and Y.-P. Sun, *RSC Adv*., 2014, **4**, 10791-10807; (b) P. G. Luo, S. Sahu, S.-T. Yang, S. K. Sonkar, J. Wang, H. Wang, G. E. LeCroy, L. Cao and Y.-P. Sun, *J. Mater. Chem. B*, 2013, **1**, 2116-2127.

4 (a) A. Shakhbazau, M. Mishra, T. Ho Chu, C. Brideau, K. Cummins, S. Tsutsui D. Shcharbin, S. Mignani, J.-P. Majoral, M. Blanchard-Desce, M. Bryszewska, V. W. Yong, P. Stys, J. van Minnen, *Macromol. Biosci*. 2015, **15**, 1523–1534. (b)) R. K. Tathavarty, M. Parent, M. H. V. Werts, S. Gmouh, A.-M Caminade, L Moreaux, S Charpak, J-P. Majoral, M. Blanchard-Desce, *Angew. Chem. Int. Ed*., 2006, **45**, 4645-4648.

5 (a) S. Fery-Forgues, *Nanoscale*, 2013, **5**, 8428-8442. (b) E. Genin, Z. Gao, J. A. Varela, J. Daniel, T. Bsaibess, I. Gosse, L. Groc, L. Cognet, M. Blanchard-Desce, *Adv. Mater*. 2014, **26**, 2258–2261.

6 L. D. Lavis, R. T. Raines, *ACS Chem. Biol*., 2008, **3**, 142-155; (b) R. N. Kumar, V. Bhalla and M. Kumar, *Chem. Commun*., 2015, **51**, 15614-15628; (c) Chendong Ji, Yang Zheng, Jie Li, Jie Shen, Wantai Yang and Meizhen Yin, *J. Mater. Chem. B*, 2015, **3**, 7494-7498; (d) B. A. D. Neto, P. H. P. R. Carvalho and J. R. Correa, *Acc. Chem. Res*., 2015, **48**, 1560−1569; (e) I. López-Duarte, P. Chairatana, Y. Wu, J. Pérez-Moreno, P. M. Bennett, J. E. Reeve, I. Boczarow, W. Kaluza, N. A. Hosny, S. D. Stranks, R. J. Nicholas, K. Clays, M. K. Kuimova and H. L. Anderson, *Org. Biomol. Chem*., 2015, **13**, 3792-3802; (f) A. Romieu, *Org. Biomol. Chem*., 2015, **13**, 1294-1306; (g) H. M. Kim and B. R. Cho, *Chem. Rev*., 2015, **115**, 5014-5055; (h) A. T. Wrobel, T. C. Johnstone, A. D. Liang, S. J. Lippard and P. Rivera-Fuentes, *J. Am. Chem. Soc*., 2014, **136**, 4697-4705; (i) Z. Guo, S. Park, J. Yoon and I. Shin, *Chem. Soc. Rev*., 2014, **43**, 16–29.

7 (a) G. S. Loving, M. Sainlos and B. Imperiali, *Trends Biotechnol*., 2010, **28**, 73-83; (b) A. S. Klymchenko and Y. Mely, *Prog. Mol. Biol. Transl. Sci*., 2013, **113**, 35-58; (c) Z. Yang, J. Cao, Y. He, J. H. Yang, T. Kim, X. Peng and J. S. Kim, *Chem. Soc. Rev*., 2014, **43**, 4563-4601. 2 (d) G. Weber and F. J. Farris, *Biochemistry*, 1979, **18**, 3075-3078; (e) D. J. Cowley, *Nature*, 1986, **319**, 14-15; (f) R. B. MacGregor and G. Weber, *Nature*, 1986, **319**, 70-73; (g) A. Jacobson, A. Petric, D. Hogenkamp, A. Sinur and J. R. Barrio, *J. Am. Chem. Soc*., 1996, **118**, 5572-5579; (h) B. E. Cohen, T. B. McAnaney, E. S. Park, Y. N. Jan, S. G. Boxer and L. Y. Jan, *Science*, 2002, **296**, 1700-1703; (i) K. Gaus, E. Gratton, E. P. W. Kable, A. S. Jones, I. Gelissen, L. Kritharides and W. Jessup, *Proc. Natl. Acad. Sci. U. S. A*., 2003, **100**, 15554-15559; (j) H. M. Kim, B. H. Jeong, J.-Y. Hyon, M. J. An, M. S. Seo, J. H. Hong, K. J. Lee, C. H. Kim, T. Joo, S.-C. Hong and B. R. Cho, *J. Am. Chem. Soc*., 2008, **130**, 4246-4247; (k) H. M. Kim, M. J. An, J. H. Hong, B. H. Jeong, O. Kwon, J.-Y. Hyon, S.-C. Hong, K. J. Lee and B. R. Cho, *Angew. Chem., Int. Ed*., 2008, **47**, 2231-2234; (l) A. S. Klymchenko and R. Kreder, *Chem. Biol*., 2014, **21**, 97-113.

8 (a) F. Terenziani, A. Painelli, C. Katan, M. Charlot and M. Blanchard-Desce, *J. Am. Chem. Soc*., 2006, **128**, 15742-15755; (b) C.-H. Zhao, A. Wakamiya, Y. Inukai and S. Yamaguchi, *J. Am. Chem. Soc*., 2006, **128**, 15934-15935; (c) J. Do, J. Huh and E. Kim, *Langmuir*, 2009, **25**, 9405-9412; (d) E. L. Spitler, J. M. Monson and M. M. Haley, *J. Org. Chem*., 2008, **73**, 2211-2223; (e) W. V. Moreshead, O. V. Przhonska, M. V. Bondar, A. D. Kachkovski, I. H. Nayyar, A. E. Masunov, A. W. Woodward and K. D. Belfield, *J. Phys. Chem. C*, 2013, **117**, 23133-23147; (f) D. H. Friese, A. Mikhaylov, M. Krzeszewski, Y. M. Poronik, A. Rebane, K. Ruud and D. T. Gryko, *Chem. Eur. J*., 2015, **21**, 18364-18374; (g) A. Rebane, M. Drobizhev, N. S. Makarov, G. Wicks, G. P. Wnuk, Y. Stepanenko, J. E. Haley, D. M. Krein, J. L. Fore, A. R. Burke, J. E. Slagle, D. G. McLean and T. M. Cooper, *J. Phys. Chem. A*, 2014, **118**, 3749-3759.

9 S. Singha, D. Kim, B. Roy, S. Sambasivan, H. Moon, A. S. Rao, J. Y. Kim, T. Joo, J. W. Park, Y. M. Rhee, T. Wang, K. H. Kim, Y. H. Shin, J. Jung and K. H. Ahn, *Chem. Sci*., 2015, **6**, 4335.

10 (a) A. C. Rochat, L. Cassar and A. Iqbal, Preparation of pyrrolo-(3,4-*c*) pyrroles Eur. Pat. Appl. 94911, **1983**; (b) A. Iqbal, M. Jost, R. Kirchmayr, J. Pfenninger, A. Rochat and O. Wallquist, *Bull. Soc. Chim. Belg*., 1988, **97**, 615; (c) Z. M. Hao and A. Iqbal, *Chem. Soc. Rev*., 1997, **26**, 203; (d) J. S. Zambounis, Z. Hao and A. Iqbal, *Nature*, 1997, **388**, 131; (e) O. Wallquist and R. Lenz, *Macromol. Symp*., 2002, **187**, 617; (f) A. Iqbal, L. Cassar, A. C. Rochat, J. Pfenninger and O. Wallquist, *J. Coat. Technol*., 1988, **60**, 37; (g) D. G. Farnum, G. Mehta, G. G. I. Moore and F. P. Siegal, *Tetrahedron Lett*., 1974, **29**, 2549.

11 (a) S. Qu, C. Qin, A. Islam, Y. Wu, W. Zhu, J. Hua, H. Tian and L. Han, *Chem. Commun*., 2012, **48**, 6972; (b) S. Qu and H. Tian, *Chem. Commun.*, 2012, **48**, 3039 and references cited therein; (c) C. B. Nielsen, M. Turbiez and I. McCulloch, *Adv. Mater.*, 2013, **13**, 1859 and references cited therein; (d) S.-Y. Liu, M.-M. Shi, J.-C. Huang,

Z.-N. Jin, X.-L. Hu, J.-Y. Pan, H.-Y. Li, A. K.-Y. Jen and H.-Z. Chen, *J. Mater. Chem. A*, 2013, **1**, 2795; (e) Y.-H. Jeong, C.-H. Lee and W.-D. Jang, *Chem. Asian J*., 2012, **7**, 1562; (f) E. Q. Guo, P. H. Ren, Y. L. Zhang, H. C. Zhang and W. J. Yang, *Chem. Commun*., 2009, 5859.

12 M. Vala, M. Weiter, J. Vynuchal, P. Toman and S. Lunak, *J. Fluoresc*., 2008, **18**, 1181.

13 L. Burgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H. J. Kirner and C. Winnewisser, *Adv. Mater*., 2008, **20**, 2217; (b) M. Tantiwiwat, A. Tamayo, N. Luu, X. D. Dang and T. Q. Nguyen, *J. Phys. Chem. C*, 2008, **112**, 17402; (c) S. L. Suraru, U. Zschieschang, H. Klauk and F. Würthner, *Chem. Commun*., 2011, **47**, 1767; (d) L. Burgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner and C. Winnewisser, *Adv. Mater*., 2008, **20**, 2217; (e) W. S. Yoon, S. K. Park , I. Cho , J.-A. Oh , J. H. Kim, and S. Y. Park, *Adv. Funct. Mater*., 2013, **23**, 3519.

14 (a) B. Tieke, A. R. Rabindranath, K. Zhang and Y. Zhu, *Beilstein J. Org. Chem.*, 2010, **6**, 830; (b) M. M. Wienk, M. Turbiez, J. Gilot and R. A. J. Janssen, *Adv. Mater*., 2008, **20**, 2556; (c) K. H. Hendriks, W. Li, M. M. Wienk and R. A. J. Janssen, *Adv. Energy Mater*., 2013, **3**, 674; (d) A. L. Kanibolotsky, F. Vilela, J. C. Forgie , S. E. T. Elmasly, P. J. Skabara, K. Zhang, B. Tieke, J. McGurk, C. R. Belton, P. N. Stavrinou and D. D. C. Bradley, *Adv. Mater*., 2011, **23**, 2093; (e) H. Y. Woo, D. Korystov, A. Mikhailovsky, T.-Q. Nguyen and G C. Bazan, *J. Am. Chem. Soc.*, 2005, **127**, 13794; (f) H. Y. Woo, B. L., B. Kohler, D. Korystov, A. Mikhailovsky and G. C. Bazan, *J. Am. Chem. Soc*., 2005, **127**, 14721; (g) Y. Li, P. Sonar, L. Murphy and W. Hong, *Energy Environ. Sci*., 2013, **6**, 1684; (h) K. H. Hendriks, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk and R. A. J. Janssen, *Angew. Chem. Int. Ed*., 2013, **52**, 8341; (i) R. C. Coffin, J. Peet, J. Rogers and G. C. Bazan, *Nat. Chem*., 2009, **1**, 657.

15 (a) T.-J. Ha, P. Sonar and A. Dodabalapur, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9735; (b) P. Sonar, T.-J. Ha and A. Dodabalapur, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7475; (c) P. Sonar, J.-M. Zhuo, L.-H. Zhao, K.-M. Lim, J. Chen, A. J. Rondinone, S. P. Singh, L.-L. Chua, P. K. H. Ho and A. Dodabalapur, *J. Mater. Chem.*, 2012, **22**, 17284; (d) Y. Li, P. Sonar, S. P. Singh, Z. E. Ooi, E. S. H. Lek and M. Q. Y. Loh, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7162; (e) P. Sonar, S. P. Singh, E. van L. Williams, Y. Li, M. S. Soh and A. Dodabalapur, *J. Mater. Chem.*, 2012, **22**, 4425; (f) M. Tantiwiwat, A. Tamayo, N. Luu, X. D. Dang and T. Q. Nguyen, *J. Phys. Chem. C*, 2008, **112**, 17402; (g) O. Kwon, J. Jo, B. Walker, G. C. Bazan and J. H. Seo, *J. Mater. Chem. A*, 2013, **1**, 7118.

16 M. Kirkus, S. Knippenberg, D. Beljonne, J. Cornil, R. A. J. Janssen and S. C. J. Meskers, *J. Phys. Chem. A*, 2013, **117**, 2782.

17 (a) T. Potrawa and H. Langhals, *Chem. Ber*., 1978, **120**, 1075; (b) H. Langhals, T. Potrawa, H. Nöth and G. Linti, *Angew. Chem.*, 1989, **101**, 497; (c) H. Langhals, S. Demmig and T. Potrawa, *J. Prakt. Chem.*, 1991, **333**, 733; (d) P. Edman, L. B.-A. Johansson and H. Langhals, *J. Phys. Chem.*, 1995, **99**, 8504; (e) M. Vala, M. Weiter, J. Vyňuchal, P. Toman and S. Luňák Jr., *J. Fluorescence*, 2008, **18**, 1181; (f) S. Luňák Jr., M. Vala, J. Vyňuchal, I. Ouzzane, P. Horáková, P. Možíšková, Z. Eliáš and M. Weiter, *Dyes Pigm.*, 2011, **91**, 269. (g) I.-P. Lorenz, M. Limmert, P. Mayer, H. Piotrowski, H. Langhals, M. Poppe and K. Polborn, *Chem. Eur. J*., 2002, **8**, 4047; (h) J. Zhang, D.-Y. Kang, S. Barlow and S. R. Marder, *J. Mater. Chem*., 2012, **22**, 21392; (i) A. Purc, M. Banasiewicz, E. Glodkowska-Mrowka and D. T. Gryko, *J. Mat. Chem. C*, 2016, **4**, DOI: 10.1039/C5TC03190G.

18 (a) S. Stas, J.-Y. Balandier, V. Lemaur, O. Fenwick, G. Tregnago, F. Quist, F. Cacialli, J. Cornil and Y. H. Geerts, *Dyes Pigm.*, 2013, **97**, 198; (b) H. Bürckstümmer, A. Weissenstein, D. Bialas and F. Würthner, *J. Org. Chem*., 2011, **76**, 2426; (c) J. Liu, B. Walker, A. Tamayo, Y. Zhang and T.-Q. Nguyen, *Adv, Func. Mater.*, 2013, **23**, 47; (d) R. S. Szabadai, J. Roth-Barton, K. P. Ghiggino, J. M. White and D. J. D. Wilson, *Aust. J. Chem.*, 2014, **67**, 1330–1337; (e) A. Purc, K. Sobczyk, Y. Sakagami, A. Ando, K. Kamada and D. T. Gryko, *J. Mater. Chem. C*, 2015, **3**, 742; (f) M. Grzybowski, E. Glodkowska-Mrowka, V. Hugues, W. Brutkowski, M. Blanchard-Desce and D. T. Gryko, *Chem. Eur. J*., 2015, **21**, 9101-9110.

19 (a) G. M. Fischer, A. R. Ehlers, A. Zumbusch and E. Daltrozzo, *Angew. Chem., Int. Ed*., 2007, **46**, 3750; (b) G. M. Fischer, M. Isomaki-Krondahl, I. Gottker-Schnetmann, E. Daltrozzo and A. Zumbusch, *Chem.–Eur. J*., 2009, **15**, 4857; (c) G. M. Fischer, C. Jungst, M. Isomaki-Krondahl, D. Gauss, H. M. Moller, E. Daltrozzo and A. Zumbusch, *Chem. Commun*., 2010, **46**, 5289; (d) G. M. Fischer, M. K. Klein, E. Daltrozzo and A. Zumbusch, *Eur. J. Org. Chem*., 2011, 3421; (e) S. Wiktorowski, G. M. Fischer, M. J. Winterhalder, E. Daltrozzo and A. Zumbusch, *Phys. Chem. Chem. Phys*., 2012, **14**, 2921.

20 (a) S. Shimizu, T. Iino, Y. Araki and N. Kobayashi, *Chem. Commun*., 2013, **49**, 1621; (b) W. Yue, S.-L. Suraru, D. Bialas, M. Muller and F. Würthner, *Angew. Chem. Int. Ed*., 2014, **53**, 6159; (c) S. Shimizu, T. Iino, A. Saeki, S. Seki and N Kobayashi, *Chem. Eur. J*., 2015, **21**, 2893-2904.

21 (a) M. Grzybowski, E. Glodkowska-Mrowka, T. Stoklosa and D. T. Gryko, *Org. Lett*., 2012, **14**, 2670; (b) M. Grzybowski, V. Hugues, M. Blanchard-Desce and D. T. Gryko, *Chem. Eur. J*., 2014, **20**, 12493. (c) D. T. Gryko, M. Grzybowski, P. Hayoz and A. Jeżewski, BASF SE, Patent Appl. PCT/EP2014/054060, 2013.

22 (a) E. Q. Guo, P. H. Ren, Y. L. Zhang, H. C. Zhang and W. J. Yang, *Chem. Commun*., 2009, 5859; (b) C. Yang, M. Zheng, Y. Li, B. Zhang, J. Li, L. Bu, W. Liu, M. Sun, H. Zhang, Y. Tao, S. Xue and W. Yang, *J. Mater. Chem. A*, 2013, **1**, 5172; (c) H. Ftouni, F. Bolze and J.-F. Nicoud, *Dyes Pigm.*, 2013, **97**, 77; (d) H. Ftouni, F. Bolze, H. de Rocquigny and J.-F. Nicoud, *Bioconjugate Chem*., 2013, **24**, 942.

23 B. Chen, Y. Yang, P. Cheng, X. Chen, X. Zhan and J. Qin, *J. Mater. Chem. A*, 2015, **3**, 6894.

24 M. Grzybowski and D. T. Gryko, *Adv. Opt. Mat*., 2015, **3**, 280-320.

25 D. F. Friese, R. Bast and K. Ruud, *ACS Phot.*, 2015, **2**, 572.

26 a) M. A. Albota, C. Xu, W. W. Webb, *Appl. Opt.* **1998**, *37*, 7352–7356; b) C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481–491.

27 M. H. V. Werts, N. Nerambourg, D. Pélégry, Y. Le Grand, M. Blanchard-Desce, *Photochem. Photobiol. Sci.* **2005**, *4*, 531–538.

28 C. Katan, S. Tretiak, M. H. V. Werts, A. J. Bain, R. J. Marsh, N. Leonczek, N. Nicolaou, E. Badaeva, O. Mongin, M. Blanchard-Desce, *J. Phys. Chem. B* **2007**, *111*, 9468–9483.

29 A. D. Becke, *J. Chem. Phys*., 1993, **98** , 5648.

30 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1989, **100**, 5829.

31 *TURBOMOLE* **V6.6** 2014, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

32 K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskov, U. Ekstrøm, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I.-M. Høyvik, M. F. Iozzi, B. Jansík, H. J. Aa. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawlowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. V. Rybkin, P. Sałek, C. C. M. Samson, A. Sánchez de Merás, T. Saue, S. P. A. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. D. Wilson, M. Ziolkowski, H. Ågren, The Dalton quantum chemistry program system,*WIREsComput. Mol. Sci.*, 2013, **4**, 269.

33 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51

34 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007

Graphical abstract

Donor-acceptor type π-expanded diketopyrrolopyrrole behaves as non-centrosymmetric as far as linear optical properties are concerned but as 'pseudo-symmetric' for two-photon absorption.