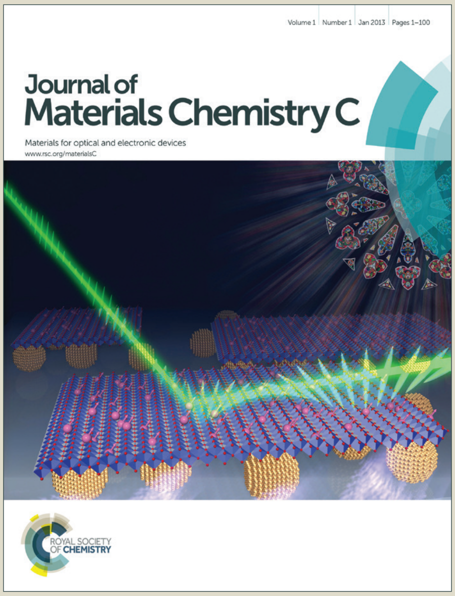
Journal of Materials Chemistry C

Accepted Manuscript



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ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Strategy towards large two-photon absorption cross-sections for diketopyrrolopyrroles

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Three quadrupolar donor-acceptor-donor compounds bearing diketopyrrolopyrroles as a central core and exceptionally electron-rich diarylaminofurans and dialkylaminobenzofuran as donors, were designed. Straightforward synthesis afforded these dyes in good overall yield. These donor-acceptor-donor systems turned out to be strong red-emitters with fluorescence extending well into NIR region. Two-photon brightness (850-1900 GM) was found to be larger than for any previously studied diketopyrrolopyrroles dye.

Introduction

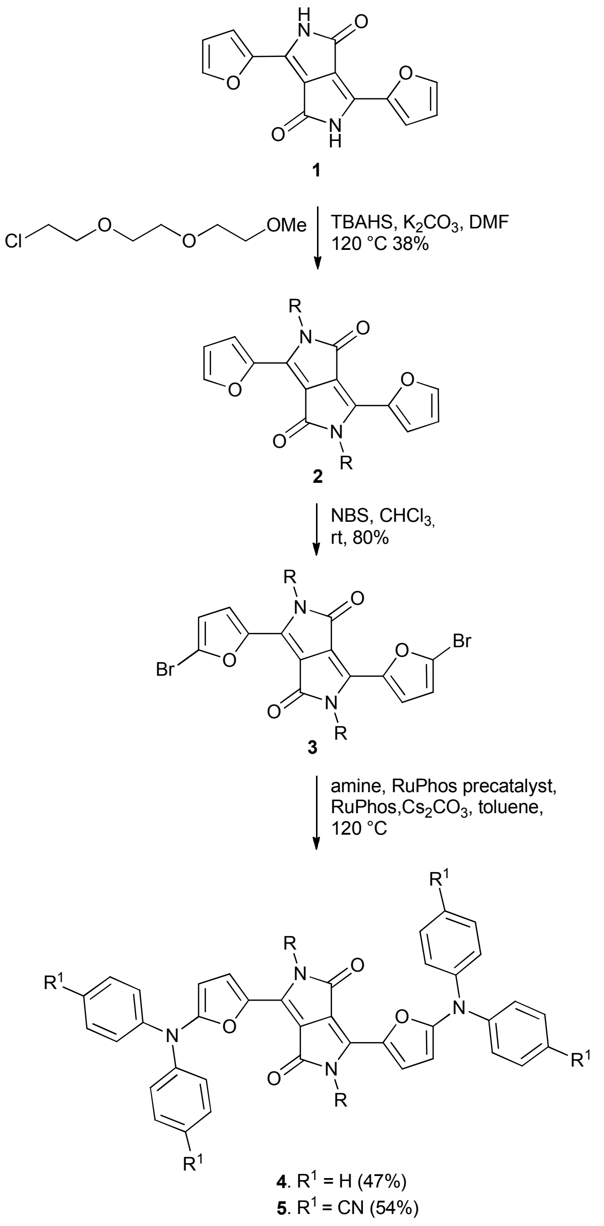
Diketopyrrolopyrroles (DPPs) in addition to rhodamines and fluoresceins are perhaps the most easily synthesizable among strongly absorbing dyes.[1] The combination of their straightforward synthesis from aromatic nitriles and dialkyl succinates and superb optical properties resulted in the renaissance of diketopyrrolopyrroles as functional dyes in last decade.[2] Since expiring of the key patent in 2003, they underwent transformation from high-quality pigments to the most popular dyes in organic electronics.[3] With applications streaming from organic field-effect transistors (OFET),[4] bulk-heterojuction solar cells,[3,4b,5] to dye-sensitized solar cells[6] they became 'working horse' of materials chemistry.[7] It is well-known that for *N*,*N*'-dialkyl-DPPs the mean angle between benzene ring and diketopyrrolopyrrole core is ~30 degrees.[8] It results in the reduced overlap of the corresponding orbitals, hence rather moderate influence of substituents on the absorption and emission.[2c,7] Situation changes rapidly if benzene rings are replaced with thiophene. The mean angle between thiophene and DPP-core is only 7 degrees,[9] and as a result attachment of additional thiophene moieties results in a bathochromic shift of absorption (hence emission).[9b] An alternative way towards modifying photophysical properties of DPPs, explored by the groups of Daltrozzo, Kobayashi, Würthner and ours is *via* π-expanding of their chromophore.[10] The electron-deficient core of diketopyrrolopyrrole is perfectly suited for the construction of quadrupolar molecules possessing general structure D-A-D and potentially large two-photon absorption (TPA) cross-sections (σ_2).[11] Yang and co-workers were first to explore this opportunity and for *N*,*N*-dialkylated bis(triphenylamino)DPP they measured σ_2 = 1200 GM (at 810 nm).[7b] Analogous DPPs possessing alkoxyphenyl substituents were investigated by Bolze and co-workers.[12] The aim of this manuscript was to increase two-photon absorption cross-section and two-photon brightness *via* allowing peripheral amino groups to stronger interact with the core *via* replacing of benzene linkers with aromatic five-membered rings. Herein we would like to present the results of this work.

Design and synthesis

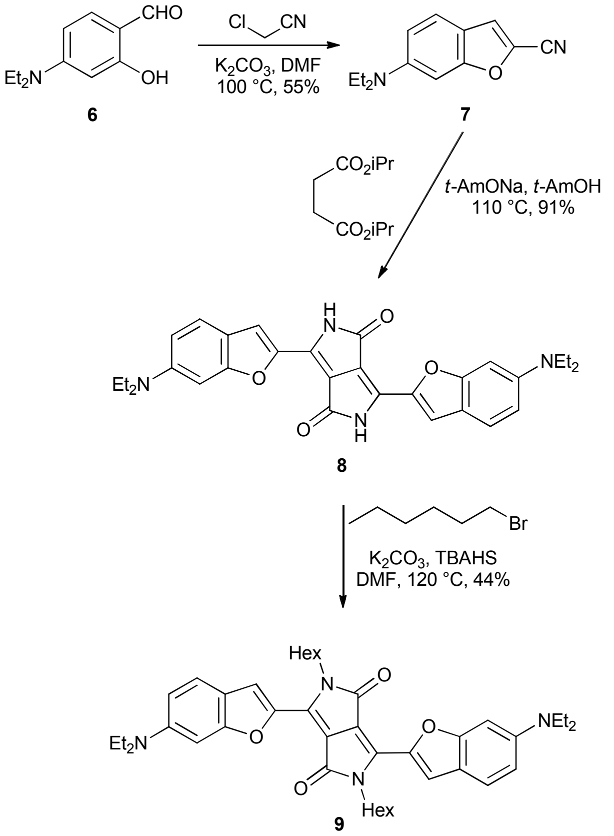
We have chosen furan as the key building blocks for three reasons: (1) Literature data revealed that the mean angle between furan and DPP-core is as low as 0.9 degree.[8] (2) Furan is more electron-rich than thiophene. (3) Known furan- and benzofuran-derived DPPs have higher fluorescence quantum yield (Φ_{fl})[10g] than corresponding derivatives of thiophene and benzothiophene. Taken together these facts should positively contribute to increasing donor-acceptor interaction in designed dyes.

Thus, we targeted furan and benzofuran derived diketopyrrolopyrroles, possessing different types of amino groups as additional electron-donors. Well-known DPP **1** prepared from 2-cyanofurane has been chosen as starting material (Scheme 1). After alkylation with 2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl chloride, compound **2** was brominated under standard conditions giving **3**, which was subjected to optimized conditions for Buchwald-Hartwig reaction[13] with diphenylamine and di(4-cyanophenyl)amine. Quadrupolar DPPs **4** and **5** were obtained in 47% and 54% yield respectively (Scheme 1).

Heating 4-(diethylamino)-2-hydroxybenzaldehyde (**6**) in DMF with chloroacetonitrile as an alkylating agent in presence of anhydrous potassium carbonate at the temperature 100 °C yielded the required substituted cyano-benzofuran **7** (Scheme 2). In the next step, compound **7** was used in DPP synthesis following the standard procedure with diisopropyl succinate and sodium *tert*-amylate in *tert*-amyl alcohol.[1a] Surprisingly high yield (91%), in spite of electron-rich character of the benzofuran moiety can only be explained by the lack of steric hindrance in proximity to CN group. Finally DPP **8** was *N*-alkylated with n-bromohexane under typical condition[14] in DMF in presence of potassium carbonate, however the reaction time was longer and tetrabutylammoniumbisulfate (TBAHS) was added as a phase-transfer catalyst.



Scheme 1.



Scheme 2.

Optical properties

The UV visible absorption (i.e. one-photon absorption, OPA) and (OPA-induced) fluorescence spectra of compounds **4**, **5** and **9** are shown in Fig. 1 and the spectroscopic parameters of the linear optical properties are summarized in Table 1. All compounds showed a sharp absorption band in the red and deep-red wavelength region (590-650 nm). The characteristic feature is very high molar absorption coefficient of dye **9** (~140,000 M^{-1} cm^{-1}), much higher than typically for DPPs and for previously published benzofuranyl-DPPs.[10g] The position of absorption maximum depends on the π-extension of the system and electron-donating ability of the peripheral unit. The absorption maximum of **5** shows blue shift from that of **4**, as expected from the reduced electron-donating ability of the peripheral unit with CN groups for **5**. On the other hand, for **9** the absorption maximum is red-shifted compared to other two, which can be explained with the π-extension by the benzofuranyl group. These results are consistent with the reported result of the compounds bearing the furanyl π-bridge and benzofuranyl and benzothienyl peripherals without strong donor group (616 and 620 nm in CH_2Cl_2);[15] their maxima are located between that of **4** and **9**.

The fluorescent maxima of **4**, **5** and **9** are located in the red and deep-red region (630-680 nm) and stretch into the NIR region. Each fluorescence band is in the mirror image relation to the corresponding absorption band with moderate Stokes shift (~2000 cm^{-1}), suggesting a small conformational change in the excited state. Fluorescence quantum yield of compounds **4**, **5** and **9** is high (>0.50) regardless the solvent studied. Emission is the strongest in the case of dye **5** bearing di(4-

cyanophenyl)amine units and the weakest for the compound bearing very electron-rich 6-diethylaminofuryl substituents.

Table 1.

Cmpd	Solvent	Absorption max	Molar absorption coefficient	Fluorescence max	fluorescence quantum yield Φ_{fl}^{a}
4	toluene	615	70 000	639	0.63
	THF	613	74 000	638	0.49
	DCM	622	77 000	643	0.79
5	toluene	585	29 000	629	0.74
	THF	591	54 000	629	0.60
	DCM	594	60 000	628	0.70
9	toluene	650	138 000	679	0.55
	THF	647	138 000	668	0.57
	DCM	658	134 000	689	0.55

[a] Cresyl violet as a reference

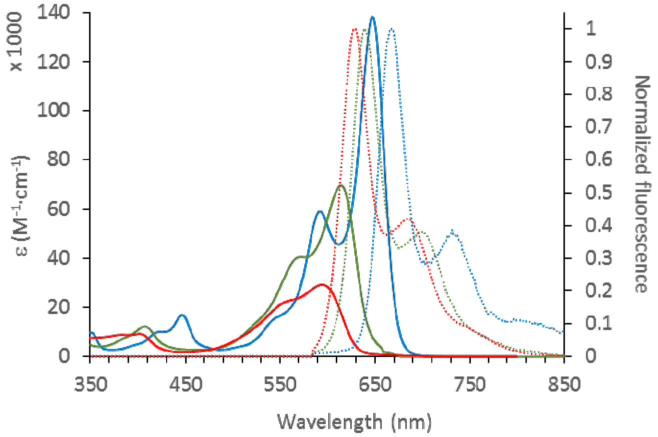


Fig. 1. Absorption (solid lines) and fluorescence (dotted lines) emission spectra of **4** (green), **5** (red) and **9** (blue) in toluene.

Fluorescence decays of compounds **4**, **5** and **9** in CH_2Cl_2 were measured by the TCSPC method to know their dynamical properties. The decay curve consists of two components (Fig. 2) for all compounds. The fast components (lifetime of ~3 ns) are dominant (>87%, Table 2), consisting with the high fluorescence quantum yield of the compounds.

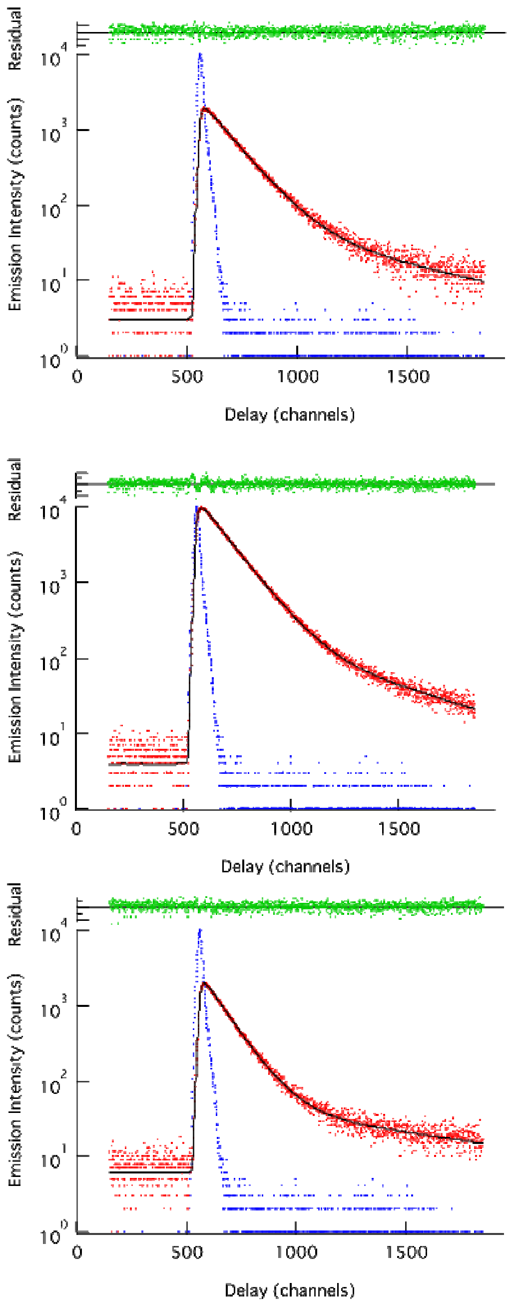


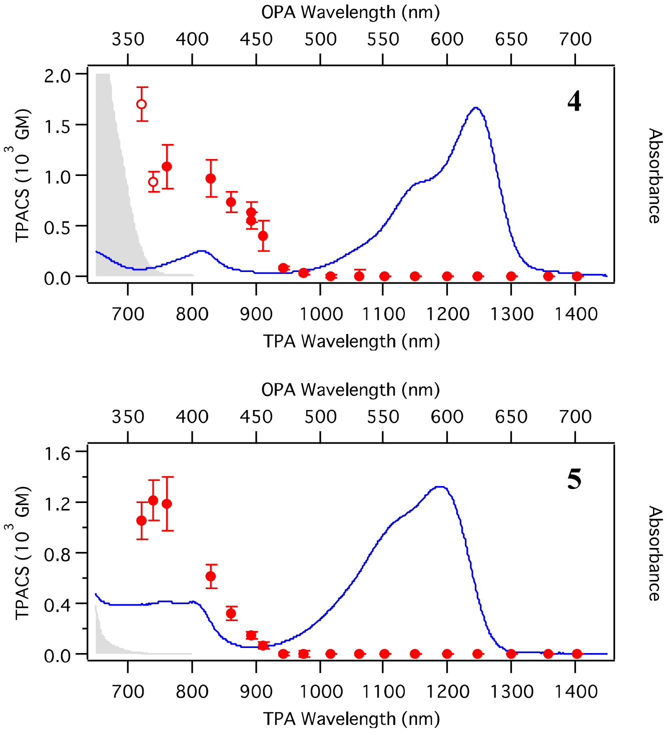
Fig. 2. Fluorescence decay data of **4** (top), **5** (middle), and **9** (bottom) in CH_2Cl_2. Excited at 374 nm.

Table 2. Fluorescence lifetime data by the TCSPC measurements.

Cmpd	τ_1	τ_2	χ2
4	3.35 ±0.02 ns (88.1%)	14.6 ±0.4 ns (11.9%)	1.16
5	3.25 ±0.01 ns (93.4%)	13.8 ±0.2 ns (6.62%)	1.20
9	2.74 ±0.01 ns (87.4%)	20.3 ±0.6 ns (12.6%)	1.15

TPA spectrum of the solutions of compound **4**, **5** and **9** in CH_2Cl_2 was measured by the femtosecond open-aperture Z-scan method (Fig. 3). Obtained parameters are tabulated in Table 3 with notes. For all samples, TPA bands were observed at wavelengths of 750–1000 nm. Initially, deformed Z-scan traces were observed for **9** and **4** in these TPA bands. The deformation was successfully minimized by stirring the solution and by reducing the excitation power (*see ESI*). The TPA spectra were obtained from such conditions. The peaks values of TPA cross section are σ_2 =1100±220 GM at 760 nm for **4**, 1200±100 GM at 740 nm for **5** and 3400±550 GM at 860 nm for **9**. These values are large as the size of molecules, especially for **9**. Given the high fluorescence quantum yields measured in CH_2Cl_2, the overall two-photon brightness (σ_2 Φ_{fl}) for quadrupolar dyes **4**, **5** and **9** is 850-1900 GM. These values are much higher than those obtained previously by Yang and Bolze (100-500 GM).[7b,12]

Moreover, at the short wavelength closed to or overlapping with the tail of OPA (750 nm or shorter, as shown by gray area in Fig. 3), significant increase in σ_2 was observed for all compounds. For compound **9**, σ_2 is up to a huge value of 19,000 GM (*see Fig. S2.4 in ESI*). The increase can be explained by resonance enhancement or double resonance.[16]. For dye **4**, saturation of OPA (saturable absorption, SA) was also observed at three wavelengths (*see ESI*). The σ_2 data for the wavelengths was obtained after elimination of the SA effect (open circles in Fig. 3).



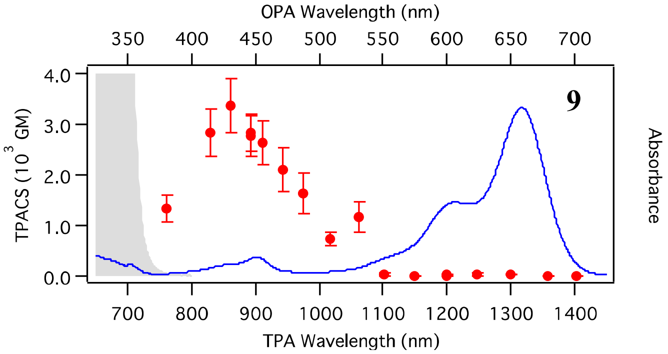


Fig. 3. TPA spectrum of compound **4**, **5** and **9** in CH_2Cl_2 (filled circles) with OPA of the same sample solution (gray area, the full scale is unity in absorbnace). Data points obtained after correction of saturable absorption (see *ESI*) are shown with open circles. The OPA spectra of the diluted samples are also shown in solid curves.

Table 3. Non-linear optical data for compounds **4**, **5** and **9** in CH_2Cl_2

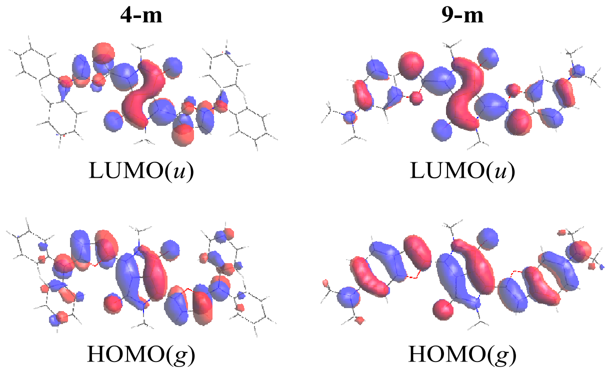
Cmpd	λ_{max} ^{2PA}	σ_2 GM	σ_2 Φ_{fl} GM
4	762	1090	860
5	739	1210	850
9	860	3370	1850

From comparison of the OPA (Fig. 1) and TPA (Fig. 3) spectra, it was shown that the transition energy of the TPA bands at 750–1000 nm overlaps that of the second OPA bands (375–500 nm). The similar trend was also reported other DPP derivatives.[10i,12] On the other hand, compounds **4**, **5** and **9** exhibited no TPA at wavelengths of 1100–1400 nm where the transition energy corresponds to the first OPA bands (550–700 nm). These spectral features indicate that the lowest one-photon allowed excited state is two-photon forbidden, which is consistent with the centrosymmetric nature of the compounds based on the Laporte selection rule, i.e. an OPA transition is allowed between the opposite parities (*gerade-ungerade* transition) while a TPA transition is forbidden. Thus, the first OPA band is the transition to an *ungerade* excited state because the ground state is always *gerade* ($1A_g$). This explanation seems to conflict to the fact that the second OPA band overlaps the TPA band in transition energy. The rational explanation is that the OPA and TPA bands cause transitions to different excited states that are degenerated or closely located in energy. To proof this idea, we performed *ab initio* quantum chemical calculation for the level structures of their excited states.

To save the computation cost, we use model molecules **4-m** and **9-m**, for which the oligoethoxy (for **4**) and hexyl (for **9**) chains attached to the DPP core are replaced with methyl groups and NEt_2 groups of the benzofuranyl groups are replaced with NMe_2 for **9**. The calculations were performed with long range corrected time-dependent density functional theory (TD-DFT) at the level of CAM-B3LYP//6-31+G(d) in gas phase (*see ESI for the details*). The result of the first four excited states are summarized in Table 4. The symmetry of the optimized structures do not match *Ci* representation exactly, nevertheless, the symmetry of the states can be assigned to S_1(*Au*-like), S_2(*Ag*-like), S_3(*Ag*-like), S_4(*Au*-like) from the symmetric pattern of the related molecular orbitals (Fig. 4). From Table 4, S_1 is widely separated in energy level from other three states (S_2–S_4) while these three are located closely to each other. Excited state having *Au*-symmetry is OPA-allowed from the ground state, thus the first and second OPA bands, which are separated largely to each other, can be assigned to *Au*-like S_1 and S_4. On the other hand, TPA-allowed excited states have *Ag*-symmetry, so the broad TPA band can be assigned to *Ag*-like S_2 and S_3 (here, the TPA transition to S_2 is probably stronger than that to S_3 because the one-electron transition of HOMO-1 → HOMO, involved in the transition to S_2, has larger orbital overlap than that of HOMO-*n* (*n*=3 for **4-m** and 5 for **9-m**) → HOMO, involved in the transition to S_3, especially in the peripheral parts). The calculated level structure, where S_2–S_4 are closely located to each other, clearly supports the idea that the TPA band (750–1000 nm) apparently overlaps the second OPA band (375–500 nm) in transition energy (i.e. they are transitions to different excited states). The calculated level structure is well explained the experimental results though the absolute transition energies are overestimated. Generally, mixing the molecular symmetries by vibronic coupling is a possible route to lead the overlap between the OPA and TPA bands in transition energy. However, the observed fact that no TPA was found at the first OPA band (Fig. 3) suggests the contribution of such mixing is not large for the present case.

Table 4. Symmetry, orbital contribution, transition energy, and oscillator strength of the model molecules of the compounds studied.

State	Symmetry nature Major orbital component	Transition energy (wavelength) Oscillator strength	
		4-m	**9-m**
S_1	*Au*-like HOMO(*g*)→LUMO(*u*)	2.4524 eV (505.6 nm) f=0.7614	2.4618 eV (503.6 nm) f=1.1350
S_2	*Ag*-like HOMO-1(*u*)→(HOMO(*g*)) →LUMO(*u*)	3.4660 eV (357.7 nm) f=0.0145	3.4905 eV (355.2 nm) f=0.0000
S_3	*Ag*-like HOMO-*n* (*u*)→(HOMO(*g*)) →LUMO(*u*) (*n* =3 for **4-m** and 5 for **9-m**)	3.7715 eV (328.7 nm) f=0.0017	3.6530 eV (339.4 nm) f=0.0000
S_4	*Au*-like HOMO-2(*g*)→LUMO(*u*)	3.8339 eV (323.4 nm) f=0.5758	3.6583 eV (338.9 nm) f=0.6079



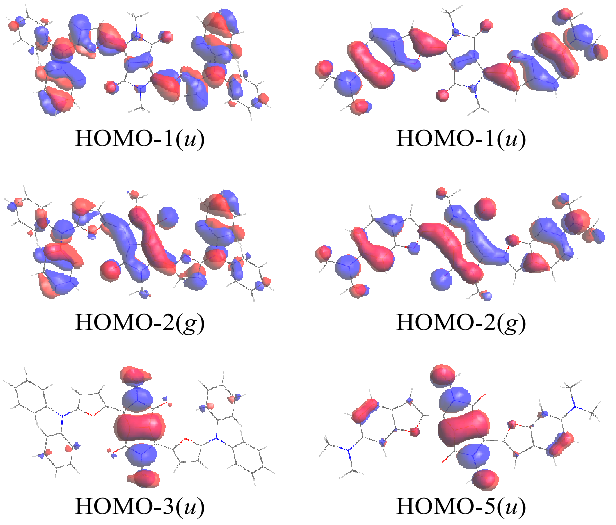


Fig. 4. Molecular orbital map of model molecules (left: **4-m**, right: **9-m**) for the related orbitals to S_1–S_4 excited states.

Experimental section

Synthesis

General: All chemicals were used as received unless otherwise noted. All reported ^{1}H NMR and ^{13}C NMR spectra were recorded on 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 except otherwise noted. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh).

2-(2-(2-(Methoxy)ethoxy)ethoxy)ethyl chloride[17], 3,6-bis(furan-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrolo-1,4-dione (**1**)[5i] and 4,4'-dicyanodiphenylamine[18] were prepared according to the literature procedures.

3,6-Bis(furan-2-yl)-2,5-di(2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl)pyrrolo[3,4-*c*]pyrrolo-1,4-dione (2) To a round-bottomed flask with condenser 3,6-bis(furan-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrolo-1,4-dione **1** (3.73 mmol, 1.00 g), TBAHS (0.19 mmol, 0.05 g) and K_2CO_3 powder (55.95 mmol, 7.73 g) was added. Then 97 ml of freshly distilled DMF was added and the mixture was vigorously stirred and heated to 120°C under an argon atmosphere. When the desired temperature was reached, 5.5 ml of 2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl chloride was added dropwise. Reaction was provided at 120°C overnight. After cooling down to room temperature, DMF was evaporated and the residue was dissolved in methylene chloride. Insoluble residue was filtered and trashed. Filtrate was washed with brine, dried over Na_2SO_4 and concentrated. Resulting precipitate was purified via flash column chromatography (CH_2Cl_2/acetone – 9:1→7:3) and crystallization from ethanol. 800 mg of desired product was obtained giving 38% yield. R_f = 0.49 (SiO_2, CH_2Cl_2/acetone, 9:1); Mp: 121-122 °C; δ_H (500 MHz, $CDCl_3$) 8.28 (d, *J* = 3.5, 2H, Fur-*H*), 7.65 (d, *J* = 1, 2H, Fur-*H*), 6.69 (d, *J* = 2, 2H, Fur-*H*), 4.37 (t, *J* = 6, 4H, CONCH_2), 3.74 (t, *J* = 6, 4H, OCH_2), 3.64 (m, 4H, OCH_2), 3.57 (t, *J* = 4.5, 8H, OCH_2), 3.48 (m, 4H, OCH_2), 3.35 (s, 6H, OCH_3); δ_C (126 MHz, $CDCl_3$) 160.8, 145.3, 144.5, 133.8, 120.2, 113.4, 106.5, 71.9, 70.7, 70.6, 69.5, 59.0, 41.5; HRMS (ESI) m/z calc. for $C_{28}H_{36}N_2O_{10}Na$: 583.2268 $(M+Na)^+$; found 583.2278.

2,5-Di(2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl)-1,4-bis(5-bromofuran-2-yl)pyrrolo[3,4-*c*]pyrrole-3,6-dione (3) To a round-bottomed flask 3,6-bis(furan-2-yl)-2,5-di(2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione **2** (0.62 mmol, 0.35 g) and chloroform (16 ml) was added. The mixture was cooled down to around 0 – 5 °C and NBS (1.31 mmol, 0.23 g) was added. Flask was covered with alumina foil. Reaction was provided in room temperature for 20 h. Reaction mixture was diluted with CH_2Cl_2 and washed with water. Organic layer was dried over Na_2SO_4 and concentrated. Resulting precipitate was purified via flash column chromatography (CH_2Cl_2/acetone − 9:1 → 4:1) and crystallization from ethanol. 350 mg of desired product was obtained giving 80% yield. R_f = 0.54 (SiO_2, CH_2Cl_2/acetone, 9:1); Mp: 122-123 °C; δ_H (500 MHz, $CDCl_3$) 8.22 (2H, d, J = 4, Fur-H), 6.62 (2H, d, J = 4, Fur-H), 4.31 (4H, m, CONCH_2), 3.75 (4H, m, OCH_2), 3.65 (4H, m, OCH_2), 3.56 (8H, m, OCH_2), 3.48 (4H, m, OCH_2), 3.35 (6H, s, OCH_3); δ_C (126 MHz, $CDCl_3$) 160.5, 146.1, 132.7, 126.4, 122.1, 115.5, 106.4, 71.9, 70.7, 70.6, 70.5, 69.4, 59.0, 41.6; HRMS (ESI) m/z calc. for $C_{28}H_{34}N_2O_{10}Br_2Na$: 739.0478 $(M+Na)^+$; found 739.0472.

2,5-Di(2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl)-1,4-bis(5-(diphenylamine)furan-2-yl)pyrrolo[3,4-*c*]pyrrole-3,6-dione (4) To a Schlenk glass RuPhos precatalyst (0.002 mmol, 2 mg), RuPhos (0.002 mmol, 1 mg), Cs_2CO_3 (0.585 mmol, 190 mg), **3** (0.097 mmol, 70 mg) and diphenylamine (0.291 mmol, 49 mg) was added under argon. Then glass was 3 times evacuated and filled with argon. 5 ml of freshly distilled toluene was added and operation of evacuation and filling with argon was repeated. Reaction was provided at 120°C overnight. To a reaction mixture water and $CHCl_3$ was added and layers were separated. Organic fraction was dried over Na_2SO_4 and concentrated. The residue was purified via flash column chromatography (CH_2Cl_2/acetone - 9:1) and crystallization from toluene/n-pentane − 1:10. 41 mg of product was obtained giving 47% yield. R_f = 0.38 (SiO_2, CH_2Cl_2/acetone, 85:15); Mp: 90-92 °C; δ_H (200 MHz, $CDCl_3$) 8.29 (d, J = 3.8, 2H, Fur-H), 7.35 (m, 8H, Ph-H), 7.17 (12H, m, Ph-H), 5.88 (2H, d, J = 3.8, Fur-H), 3.97 (4H, t, J = 5.8, CONCH_2), 3.46 (20H, m, OCH_2), 3.33 (6H, s, OCH_3); δ_C (50 MHz, $CDCl_3$) 156.7, 144.5, 130.0, 125.6, 124.6, 123.7, 98.2, 72.4, 71.0, 70.9, 70.7, 69.9, 59.4, 41.8; HRMS (ESI) m/z calc. for $C_{52}H_{54}N_4O_{10}Na$: 917.3738 $(M+Na)^+$; found 917.3723.

2,5-Di(2-(2-(2-(methoxy)ethoxy)ethoxy)ethyl)-1,4-bis(5-(4,4'-dicyanodiphenylamine)furan-2-yl)pyrrolo[3,4-c]pyrrole-3,6-dione (5) This compound was prepared similarly to **4** from 4,4'-dicyanodiphenylamine (0.388 mmol, 85 mg) Solvent for flash column chromatography: CH_2Cl_2/acetone – 9:1 → 85:15. Crystallization from ethanol. 52 mg of product was obtained giving 54% yield; R_f = 0.54 (SiO_2, CH_2Cl_2/acetone, 4:1), Mp: Decomposition > 215 °C δ_H (500 MHz, CD_2Cl_2) 8.28 (2H, d, J = 4, Fur-H), 7.67 (8H, m, Ph-H), 7.27 (8H, m, Ph-H), 6.23 (2H, d, J = 4, Fur-H), 3.98 (4H, t, J = 6, CONCH_2), 3.49 (4H, m, OCH_2), 3.41 (16H, m, OCH_2), 3.27 (6H, s, OCH_3); δ_C (126 MHz, CD_2Cl_2) δ 160.8, 153.0, 147.4, 140.3, 134.3, 132.7, 123.7, 122.3, 118.7, 108.7, 106.6, 103.7, 72.2, 70.9, 70.8, 70.7, 69.7, 58.9, 41.9; HRMS (ESI) m/z calc. for $C_{56}H_{50}N_8O_{10}Na$: 1017.3548 (M+Na)+; found 1017.3557.

6-(Diethylamino)-benzofuran-2-carbonitrile (7). 4-(Diethylamino)-2-hydroxybenzaldehyde (**6**, 0.58 g, 3.0 mmol), chloroacetonitrile (0.58 ml, 3.6 mmol) and freshly grounded K_2CO_3 (2.49 g, 18 mmol) were placed in a three-necked flask containing 15 ml of DMF. The mixture was stirred overnight at 100 °C under an argon atmosphere. The reaction mixture was cooled to the room temperature and diluted with water and $CHCl_3$. The aqueous layer was extracted with $CHCl_3$, combined organic layers were washed with water and brine and dried over $MgSO_4$. Solvents were evaporated and the product was purified using the column chromatography (SiO_2; hexanes/AcOEt 1:2). Yield: 0.37 g (55%) as yellowish oil. All spectroscopic data of isolated product correspond with literature.[19]

1,4-Diketo-3,6-di(6-(diethylamino)-2-benzofuryl)pyrrolo[3,4-*c*]pyrrole (8). Tert-amyl alcohol (15 ml), sodium (0.51 g, 22 mmol) and an catalytic amount of $FeCl_3$ were placed in a three-necked flask. The mixture was refluxed under an argon atmosphere until sodium has completely reacted. Then 6-(diethylamino)-benzofuran-2-carbonitrile (**7**, 2.14 g, 10 mmol) was added. The mixture was then heated to 110 °C and diisopropyl succinate (0.99 ml, 4.4 mmol) was added dropwise. After 16 h of reaction at 110°C, the mixture was cooled to 40 °C and 15 ml of mixture water/methanol/acetic acid (1:1:1) was added. Resulting suspension was refluxed for a few minutes and cooled to the room temperature. Precipitate of obtained green pigment was then filtered out, washed several times with hot water and methanol and dried under vacuum. Yield: 2.03 g (91%). Mp: Decomposition > 340°C; δ_H (500 MHz, $CDCl_3$:TFA-d 4:1) 8.30 (2H, s, Ar-H), 8.04 (2H, d, J = 8.6, Ar-H), 7.87 (2H, s, Ar-H), 7.51 (2H, d, J = 8.6, Ar-H), 3.87-3.67 (8H, m, NCH_2), 1.24 (12H, t, J = 6.9, CH_3); δ_C (126 MHz, CDCl3:TFA-d 4:1) 155.7, 146.4, 136.0, 133.9, 130.5, 125.8, 117.7, 115.4, 113.1, 110.9, 106.9, 55.5, 10.1; HRMS (EI) calc. for $C_{30}H_{30}N_4O_4$ (M+): 510.2275, found: 510.2267. Elemental analysis calc. (%) for $C_{30}H_{30}N_4O_4$: C 70.57, H 5.92, N 10.97; found: C 70.52, H 5.72, N 10.88.

2,5-Dihexyl-1,4-diketo-3,6-di(6-(diethylamino)-2-benzofuryl)pyrrolo[3,4-*c*]pyrrole (9). A mixture of 1,4-diketo-3,6-di(6-(diethylamino)-2-benzofuryl)pyrrolo[3,4-c]pyrrole **8** (1.53 g, 1.5 mmol), tetrabutylammoniumbisulfate (TBAHS, 51 mg, 0.05 mmol), K_2CO_3 (6.22 g, 55 mmol) and 78 ml of DMF were heated to 120 °C under an argon atmosphere. Then n-bromohexane (4.21 ml, 15 mmol) was added dropwise via syringe. The reaction mixture was stirred overnight, then cooled and diluted with water and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2, combined organic layers were washed with water and brine and dried over $MgSO_4$. Mixture was concentrated to ¼ volume, precipitate was filtered, washed with DMF and diethyl ether and crystallized from methanol. Yield: 0.90 g (44%). Mp: Decomposition > 240°C; δ_H (500 MHz, C_6D_6, 50 °C) 9.33 (2H, s, Ar-H), 7.23 (2H, d, J = 8.3, Ar-H), 6.69 (2H, d, J = 1.0, Ar-H), 6.47 (2H, dd, J_1 = 8.8, J_2 = 2.0, Ar-H), 4.41 (4H, t, J = 7.3, CONCH_2), 2.96 (8H, q, J = 7.3, NCH_2), 1.93-1.88 (4H, m, CH_2), 1.51-1.45 (4H, m, CH_2), 1.35-122 (8H, m, CH_2), 0.88-0.84 (18H, m, CH_3); δ_C (126 MHz, C_6D_6, 50 °C) δ 160.9, 158.7, 148.4, 144.2, 132.7, 122.8, 118.5, 116.4, 111.0, 107.9, 92.9, 44.5, 42.3, 31.4, 30.4, 26.6, 22.5, 13.7, 12.2; HRMS (TOF ESI) calc. for $C_{42}H_{54}N_4O_4$ (M^+): 678.4157, found: 678.4145. Elemental analysis calc. (%) for

$C_{42}H_{54}N_4O_4$: C 74.30, H 8.02, N 8.25; found: C 74.28, H 8.06, N 8.18.

Optical measurements

Fluorescence decays of the compound solution in CH_2Cl_2 were measured by the TCSPC method (a *HORIBA FluoroCube*) under air-saturated condition. Absorbance of each sample was set below 0.1 with a 1-cm cuvette at the excitation wavelength of 374 nm.

Two-photon absorption spectra were measured by the open-aperture Z-scan method[20] with a femtosecond optical parametric amplifier (*SpectraPhysics OPA-800* pumped by *Spitfire* operating at 1 kHz of repetition rate) as light source by varying the incident wavelength. The details of the setup were reported previously.[21] Typical pulse width employed was 120 fs. Rayleigh range of the setup is typically 9 mm. Solutions of **4** (0.53~2.0 mM), **5** (1.9~2.1 mM) and **9** (0.50~2.0 mM) in CH_2Cl_2 held in a 2-mm quartz cuvette were used (*see ESI for the selection of solvent*). Typical examples of the observed open-aperture traces are shown in *ESI*. Observed Z-scan traces were analyzed by the curve fitting procedure with the equation for the transmittance of sample for spatially and temporally Gaussian pulses as reported previously.[22] Since some deformed Z-scan traces were observed initially, low incident powers (<0.3 mW, corresponding less than ~50 GW/cm^2 of the on-axis peak power at the focal point) and sample stirring during the measurement were used (*see ESI for the detail*). The UV-vis absorption spectra were measured before and after the Z-scan measurements and no spectral change was found by irradiation, except for the case where the laser wavelength overlapped the OPA (<760 nm) for **9** (*see ESI for the detail*). In the cases where saturable absorption (SA) were observed at the wavelengths overlapping the OPA, the effect of SA was taken into account for analysis.[21]

Conclusions

The strategy of enhancing electronic communication by increasing planarity between the donor and acceptor moieties in diketopyrrolopyrroles and increasing electron-donating power of donor proved ideal for obtaining red-emitting fluorophores with large two-photon absorption cross-section. We have shown that by replacing the 4-aminophenyl substituents with aminofurans and aminobenzofurans, it is possible to obtain diketopyrrolopyrrole derivatives possessing intense emission, and high two-photon absorption cross-section, which eventually leads to good two-photon brightness. The synthesis of these dyes can be performed in a few steps with high overall yield. Two-photon brightness of new dyes positively compares with their bis(diphenylaminophenyl) analogs. The TPA spectra for wide range and the quantum chemical calculation clarified the level structure of the excited states and successfully explained why the TPA band always appears nearly twice the wavelengths of the second OPA band. This will lead the comprehensive understanding the TPA spectral features of the diketopyrrolo-pyrrole family.

Acknowledgement

We thank the Foundation for Polish Science (TEAM-2009-4/3). This work was partially supported by the European Commission (TOPBIO ITN), BASF-Schweiz, and a Grant-in-Aid for Scientific Research on Innovative Areas 'Stimuli-Responsive Chemical Species' (No. 25109544, KK) from MEXT, Japan and No. 25248007 (KK) from JSPS. KK thanks to Dr. N. Murase to kindly allow access the TCSPC equipment.

Notes

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Electronic Supplementary Information (ESI) available: [details of optical and computational studies, ^{1}H NMR and ^{13}C NMR spectra of all new compounds]. See DOI: 10.1039/b000000x/

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Graphical abstract:

Decorating diketopyrrolopyrroles with strongly electron-rich heterocycles led to donor-acceptor-donor architectures possessing two-photon brightness 850-1900 GM.