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ARTICLE

Internal charge transfer-dependent solvent effect in V-shaped azacyanines

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New V-shaped non-centrosymmetric dyes, possessing strongly electron-deficient azacyanine core, have been synthesized based on a straightforward two-step approach. The key step in this synthesis involves palladium-catalysed cross-coupling of dibromo-*N,N'*-methylene-2,2'-azapyridinocyanines with arylacetylenes. The resulting strongly polarized π-expanded heterocycles exhibit green to orange fluorescence and they strongly respond to changes in solvent polarity. We demonstrate that differently electron-donating peripheral groups have significant influence on the internal charge transfer, hence, on solvent effect and fluorescence quantum yield. TD-DFT calculations confirm that, in contrast to previously studied bis(styryl)azacyanines, the proximity of S_1 and T_2 states calculated for compound bearing two 4-*N,N*-dimethylaminophenylethynyl moieties establishes good conditions for efficient intersystem crossing and is responsible for its low fluorescence quantum yield. Non-linear properties have also been determined for new azacyanines and the results show that depending on peripheral groups, the synthesized dyes exhibit small to large two-photon absorption cross sections reaching 4000 GM.

Introduction

The discovery of structure-to-non-linear optical properties relationship has opened new possibilities for the application of two-photon absorbing organic materials in various fields.[1-5] Rationally designed two-photon absorbing materials are widely used in optical power limiting,[6] 3D microfabrication,[7] 3D data storage,[8,9] localized release of bio-active species[10] and multiphoton microscopy.[11] Particularly, the latter technique was proved to be useful in bioimaging, due to the high spatial resolution and low excitation energy.[12]

In order to achieve strong, two-photon-induced optical response, the following structural motifs are usually employed: D-π-A dipoles, D-π-A-π-D quadrupoles and more complex (D-π-)₃A octupoles (where D and A denote respectively electron donors and acceptors and 'π' is a π-conjugated bridge), however, materials based on porphyrins,[13,14] multi-annulenes,[15] polymers and nano-aggregates[16] have also been extensively studied. Arylamines are the most frequently used structural motif playing a role of electron donor, whereas many different electron acceptors have been tested. Cyano-, nitro- and polyfluoro- substituted benzene derivatives, azines, azoles, squaraine dyes,[17] coumarins,[18] diketopyrrolopyrroles,[19,20] and merocyanines[21] have already been proven to strongly enhance

two-photon action, but new electron acceptors are continuously developed. Needless to say, the obvious candidate for electron-deficient units are quaternary salts of six-membered aza-heterocycles – compounds predominantly studied by Vaquero and co-workers.[22] We recently contributed to this subject by introducing π-expanded azacyanine dyes into two-photon absorbing scaffolds.[23] There are several features that make *N,N'*-methylene-2,2'-azapyridinocyanines particularly interesting compounds for donor-acceptor systems: straightforward synthesis,[24-27] large two-photon brightness and, finally, good solubility in polar solvents, including aqueous solutions. The latter property can be attributed to the cationic structure and should be considered as a huge advantage over many other two-photon absorbing dyes being usually poorly water soluble π-expanded systems. Moreover, the non-linear absorption of previously presented bis(styryl)azacyanines[23] occurs in so-called "biological window", while their cationic character might favour specific interaction with particular subcellular components. Taking all above into consideration, π-expanded azacyanines seem to be promising candidates for applications in two-photon bioimaging, therefore, we decided to further explore their properties. Herein, we would like to present the synthesis and photophysical properties of new bis(phenylethynyl)azacyanines.

Results and discussion

Design and synthesis

Azacyanines are considered to be strong electron acceptors; therefore, their substitution with strong electron donors *via* π-bridge should result in the formation of typical quadrupolar D-π-A$^+$-π-D structure. To achieve this goal, we decided to follow palladium catalyzed Sonogashira-type coupling of 3,9-dibromoazacyanine **1** with phenylacetylenes **2** and **3**, substituted with electron-donating groups on phenyl ring (Scheme 1). All our previous attempts[23] resulted in the formation of complex mixture; however palladium/copper catalytic system in DMF[22i] finally led to expected products **4** and **5**. Despite the formation of multiple side-products, careful chromatography and crystallization led to the samples of analytical purity. The prepared dyes were chemically stable and were subjected to photophysical studies.
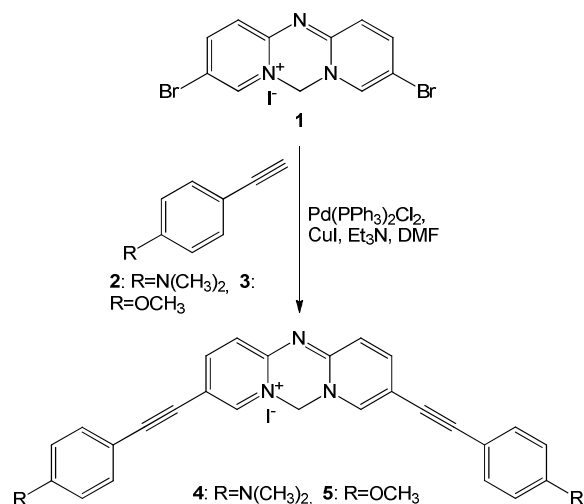
Scheme 1 The synthesis route used to obtain azacyanines **4** and **5**.

Photophysical properties

Steady-state spectroscopy

The electronic absorption and steady-state fluorescence spectra taken for compounds **4** and **5** are shown in Fig. 1 and in Fig. 2 and corresponding parameters are collected in Table 1. In comparison with parent 2,10-dimethylazacyanine, which exhibit absorption and emission maxima at 388 and 452 nm respectively,[23] both azacyanines **4** and **5** have their absorption and emission maxima bathochromically shifted by *ca.* 100 nm (see also Fig. S1 and S2 in ESI). The current dyes **4** and **5** differ from previously published ones[23] in the type of linker, in which C-C triple bond is replaced by C-C double bond. As shown by Meier[28] and Blanchard-Desce[29] such difference can have profound effect on both linear and non-linear optical properties. In particular, it was found that ethylene linker ensures improved conjugation between various parts of the molecule leading typically to stronger bathochromic shift, larger two-photon absorption cross-section and higher quantum yields.[28,29] In our case however, the comparison of optical properties of dyes **4**

and **5** reveals that both their absorption and emission is bathochromically shifted versus that of their analogues bearing
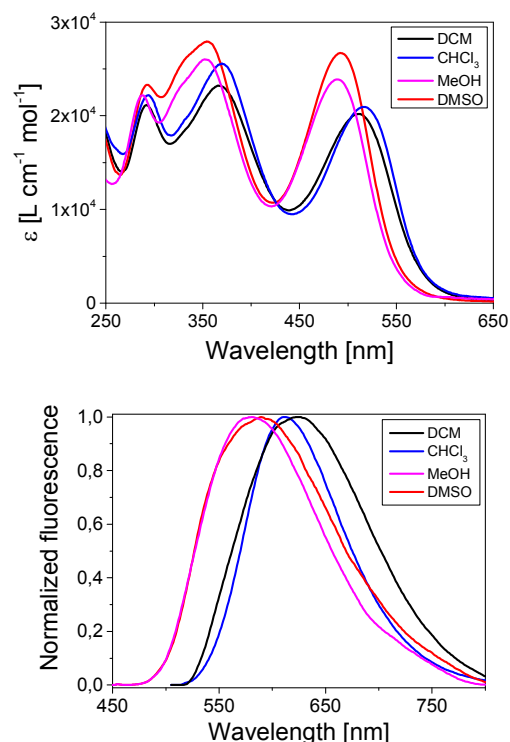
Fig. 1 Electronic absorption spectra (top) and normalized fluorescence emission spectra (bottom, λ_{ex}=490 nm) collected for **4** in all studied solvents.
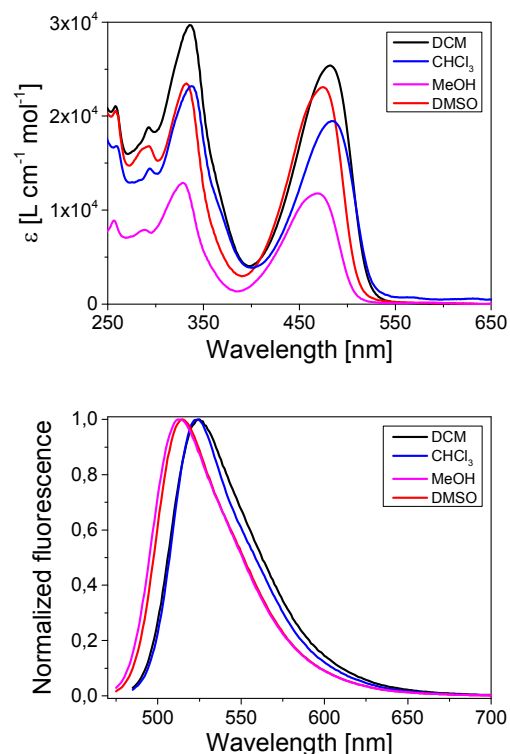
Fig. 2 Electronic absorption spectra (top) and normalized fluorescence spectra (bottom, λ_{ex}=470 nm) collected for **5** in all studied solvents.

C-C double bond[23] and the typical difference is ~20 nm. More intriguing, while fluorescence quantum yield for both dyes possessing $MeOC_6H_4$ groups are reasonably high (41% and 19%[23] respectively in $CHCl_3$) there is a striking difference for their analogues possessing more electron-donating $Me_2NC_6H_4$ groups. Indeed, while fluorescence quantum yield for previously studied compound bearing ethylene linker was 25%,[23] Φ_{fl} for dye **4** is only 3.1% in $CHCl_3$ (Table 1). The effect of solvent polarity on emission intensity is also profound. Dimethoxy-substituted cyanine **5** retains high fluorescence quantum yield (Φ_{fl}=0.53 in DMSO) characteristic for 2,10-dimethylazacyanine (Φ_{fl}=0.44 in H_2O), whereas fluorescence of dimethylamino- substituted cyanine **4** is strongly quenched (Φ_{fl} = 0.05 in DMSO).

In order to reveal the reason for such striking difference, we measured the absorption and emission spectra of **4** and **5** in four solvents of a different polarity (Table 2). We observed strong negative solvatochromism for both dyes (analogous to classical Brooker's merocyanine[30]), indicating larger stabilization of the ground state of azacyanine molecules combined with increased reorganization energy in more polar solvents, which thus increases the energy gap between the ground state and (Franck-Condon) excited state and leads to shorter wavelength of the absorbed light. This effect was particularly strong for **4**, where 20 and 46 nm hypsochromic shift of respectively absorption and emission maxima was observed in the polarity range

Table 1 Basic photophysical properties determined for **4** and **5** from steady-state experiments. λ_{abs} is the wavelength at absorption peak, ε is molar extinction coefficient determined at λ_{abs}, λ_{ex} is the excitation wavelength, λ_{em} is the wavelength at fluorescence emission peak, $\Delta\nu$ is Stokes' shift and Φ_{fl} is fluorescence quantum yield.

Dye	λ_{abs} (nm)	ε ×10⁻³ (M⁻¹ cm⁻¹)	λ_{em} (nm)		$\Delta\nu$ (cm⁻¹)	Φ_{fl} (%)
			λ_{ex1}^a nm	λ_{ex2}^b nm		
4 (CH₂Cl₂)	293	21	414			
	368	23	490	626	3600	1.0
	510	20	616			
4 (CHCl₃)	294	22	406			
	370	25.5	463	611	3000	3.1
	517	21	614			
4 (DMSO)	292	33.5				
	355	40ᶜ	435	589	3300	0.5
	492	38	463			
4 (MeOH)	288	22	426			
	352	26ᶜ	463	580	3200	0.4
	490	24	570			
5 (CH₂Cl₂)	293	19	380			
	336	30	400	525	1700	26
	482	25	524			
5 (CHCl₃)	294	14.5				
	337	23.2	524	524	1600	41
	484	19.5				
5 (DMSO)	293	17				
	332	23.5	515	515	1700	53
	474	23				
5 (MeOH)	288	8				
	330	13	512	512	1700	46
	470	12				

[a] **4** was excited at 330 nm and **5** at 350 nm, [b] **4** was excited at 470 nm and **5** at 490 nm. [c] at a shoulder at around 300 nm.

between dichloromethane and methanol.

Time-resolved spectroscopy

In order to provide further insight into the mechanism of fluorescence quenching observed for compound **4**, we executed time-resolved fluorescence spectroscopy measurements. The fluorescence decays are presented in Fig. 3a and 3b and corresponding fit parameters in Table 2. The results revealed that fluorescence decay time of azacyanine **5** is virtually unaffected by changes in solvent polarity (τ_1=2.5 ns), whereas fluorescence decay time determined for **4** is shortened in solvents of low polarity. Noticeably, two contributions could be determined. The first shorter (τ_1=0.8-1.8 ns) for locally excited state and the second longer (τ_2=5-10 ns), which can be associated with internal charge-transfer state.

As it can be seen in Table 2, in moderately low polarity solvents the major decay time contribution comes from a short living species decaying from a locally excited state, while for much more polar solvent such as methanol the longer component associated to internal charge transfer is dominating. In the case of methanol additional effect associated with hydrogen bonding may have influence on the final decay time.
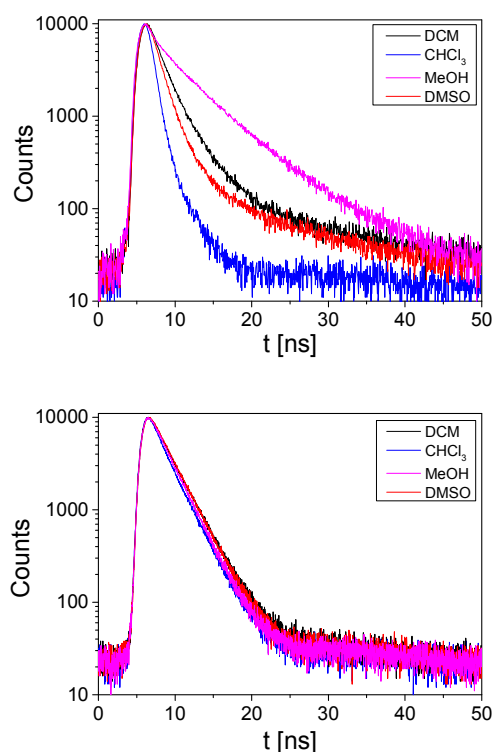
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Fig. 3 Fluorescence decays collected for compounds **4** (top) and **5** (bottom) in four solvents of different polarity.

Table 2 Basic photophysical properties determined for **4** and **5** from time-resolved experiments. A_1 and A_2 is respectively the contribution of decay time τ_1 and τ_2 in the fluorescence decay, τ_{av} is an average decay time calculated based on τ_1 and τ_2 values, k_f and k_{nr} is the rate of radiative and non-radiative processes, respectively.

Compd.	λ_{em} (nm)	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{av} (ns)	k_f (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
4[a]	490	86	1.85	14	7.55	2.6	0.04	3.73
4[b]	410	97	0.8	3	4.5	0.9	0.34	10.76
	615	98	0.6	2	6.2	0.7	0.44	13.84
4[c]	460	90	1.45	10	10	2.3	0.02	4.33
4[d]	430	20	1.3	80	5.9	5.0	0.08	1.99
5[a]	520	100	2.5	-	-	2.5	1.04	2.96
5[b]	520	100	2.5	-	-	2.5	1.64	2.36
5[c]	520	100	2.6	-	-	2.6	2.04	1.81
5[d]	520	100	2.4	-	-	2.4	1.91	2.25

[a] measured in CH_2Cl_2. [b] measured in $CHCl_3$. [c] measured in DMSO. [d] measured in MeOH.

In multifluorophoric systems a charge separation may occur depending on solvent polarity and fluorescence emission can be observed before and after the charge separation. In this case, the loss in quantum yield can be an effect of an internal charge transfer. In low polarity solvents the dye emits at shorter wavelengths from locally excited state, but as the solvent polarity increases fluorescence from internal charge-transfer state becomes visible at longer wavelength.[31] Simultaneously, the quantum yield decreases significantly for **4** when compared with **5** for which ICT was observed only in the case of rather

low polar DCM. Additionally, two contributions are observed in fluorescence decay, which again can be assigned to ICT.
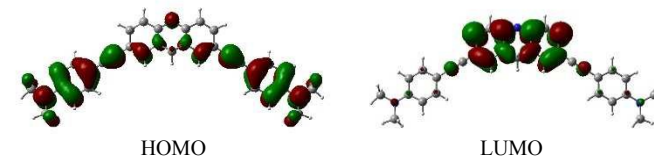
Theoretical calculations

To strengthen optical data interpretation, we decided to perform DFT calculations, including optimization of the structures of compounds **4** and **5** (as well as two previously reported bis(styryl)azacyanines[23]) in the ground and excited electronic states and the determination of the energy of electronic transitions that characterize them (Tables S1-S3). Results of TD-DFT B3LYP/6-31G(d,p) calculations of transition energies and oscillator strengths for compounds **4** and **5** are collected in Table S2, while Table S3 presents the results obtained for the structures optimized in the excited state.

A comparison of the calculated transition energies with the experimental data shows that they are a subject to systematic error, typical for TD-DFT B3LYP method applied to charge transfer systems.[32] These deviations have been an object of rational systematization in terms of the type of investigated molecular system.[33] In the case of the V-shaped azacyanies, the calculated energies of S_1 states are too low by c.a. 1500 cm^{-1} - 3000 cm^{-1}. On the other hand, the calculations well reproduce the distribution of the bands intensity in the observed absorption spectra, what is shown in Fig. S3. Theoretical results correctly reflect the experimentally determined relationship between the absorption wavelengths corresponding to the individual molecules: λ_{abs}(-NMe$_2$) > λ_{abs}(-OCH$_3$) for bis(phenylethynyl) and bis(styryl)[23] substituted azacyanines.
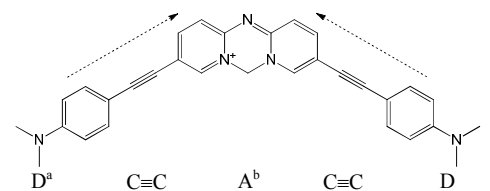
In the view of the data collected in Table 3 (with use of **4** as an example) and Table S2, substituent effect on electronic spectra of V-shaped azacyanines is correlated with the electronic charge transferred from D groups to A group at the excitation, which confirms the intuitive knowledge on the internal charge-transfer (ICT) properties of the studied systems. The calculation results qualitatively reproduce the observed solvent effects on the fluorescence spectra (blue shift with increasing polarity of the solvent). This effect is different than typically observed for conventional ICT systems. In the light of the data given in Table 3, however, it can be understood that the essence of these differences, is associated with multi-center character of the charge transfer in the V-shaped azacyanines in contrast to the two-center charge transfer between D and A in the case of typical ICT systems.

Finally, the data collected in Table S3 fits very well to the experimental results concerning the Stokes shifts, and even rate constants for radiative transition.

Table 3 Charge transfer character of the $S_0 \rightarrow S_1$ transition in V-shaped azacyanines - results of DFT B3LYP/6-31G(d,p) calculations for **4** in CH_2Cl_2. $S_0 \rightarrow S_1$ transition is described by electronic configuration (HOMO, LUMO), showed at the top. $q(S_0)$ and $q(S_1)$ characterize the distributions of charge over individual subgroups of molecule (shown above) in the ground and excited state, respectively. The δq values are the differences between them. It is seen, that electronic charge $\delta q = -0.461$ is transferred from D to A in the $S_0 \rightarrow S_1$ transition.

HOMO   LUMO

	D[a]	C≡C	A[b]	C≡C	D
$q(S_0)$	0.154	-0.063	0.818	-0.063	0.154
$q(S_1)$	0.366	-0.044	0.357	-0.044	0.366
$\delta q = q(S_1) - q(S_0)$	0.212	0.019	**-0.461**	0.019	0.212

[a] electron donor (dimethylaminophenyl moiety). [b] electron acceptor (azacyanine core).

The rationale behind the surprisingly low fluorescence quantum yield for **4** can be found in the last column of Table S2. The proximity of S_1 and T_2 states calculated for compound **4** establishes good conditions for large intersystem crossing rate constant. At the same time, such conditions are not met for related bis(styryl)azacyanines[23] possessing large fluorescence quantum yields.

Two-photon absorption measurements

Two-photon absorption was measured for compounds **4** and **5** in DCM. It turned out that in contrast to what was observed previously for analogous dyes possessing C-C double bond[23] as a linker, two-photon absorption cross-section was significantly higher (at maxima) for dye **5** bearing $MeOC_6H_4$ group (σ_2 = 4200 GM at 740 nm) while for dye **4** possessing stronger electron-donating group it was only 47 GM at 740 nm. The effects associated to the internal charge transfer as well as in the geometry of linkers can be accounted for the difference in two photon absorption.

Conclusions

Cationic, conjugated chromophores bearing D-π-A+-π-D system, can be built in straightforward manner from N,N'-methylene-2,2'-azapyridinocyanine as electron-deficient core. Strongly polarized nature of these compounds is responsible for negative solvatochromism and for large differences in their linear optical properties. They have been designed in a way that the part of the molecule, which is responsible for high polarity, is also integral part of the chromophore influencing optical properties. Most importantly, we have proved that difference in electron-donating ability between MeO and Me_2N groups has

significant influence on optical properties through determining intramolecular charge-transfer. The unusual hypsochromic shift of fluorescence with increasing polarity of the solvent can be rationalized in terms of multi-center character of the charge transfer in the V-shaped azacyanines (while in typical ICT systems it is two-center charge transfer between D and A). We also demonstrated that two-photon absorption cross-section is higher for dye possessing weaker electron-donating (i.e. methoxy) group.

Acknowledgements

Experimental

Materials and methods

All commercially available compounds were used without additional purification, unless otherwise noted. Organic solvents were purified according to generally accepted literature methods.[34] All reported NMR spectra (^1H NMR and ^{13}C NMR) were recorded on a Varian 500 spectrometer. High resolution mass spectra (HRMS) were obtained via electrospray (ESI). Chromatography was performed on silica gel 60 (230-400 mesh) and thin layer chromatography was performed on TLC plates (Merck, silica gel 60 F_{254}). Compound **1** was prepared according to previously reported procedure.[26]

Synthetic procedures

General method for the preparation of 3,9-bis(4-dimethylaminophenylethynyl)-6H-dipyrido[1,2-a:2',1'-d][1,3,5]triazin-5-ium iodide (**4**) and 3,9-bis(4-methoxyphenylethynyl)-6H-dipyrido[1,2-a:2',1'-d][1,3,5]triazin-5-ium iodide (**5**). The mixture of **1** (103 mg, 173 µmol), copper (I) iodide (6.6 mg, 35 µmol) and $Pd(PPh_3)_2Cl_2$ (13.8 mg, 17 µmol) was dissolved in dry DMF (5 mL) in Schlenk flask under the argon atmosphere. Phenylacetylene derivative (690 µmol) was added, followed by dry Et_3N (135 µL, 777 µmol) and the resulting mixture was heated at 60°C for 16 h. Then solvent was removed and the dark residue was chromatographed (SiO_2, CH_2Cl_2/MeOH, 94:6). Fractions containing desired product were evaporated and crystallized from i-PrOH, affording samples of analytical purity.

4: dark violet crystals, 51 mg, 49%. ^1H NMR (DMSO, 500 MHz): δ 8.41 (d, J = 1.8 Hz, 2H), 8.05 (dd, J = 9.0, 1.8 Hz, 2H), 7.38, 6.74 (AA'BB', J = 8.9 Hz, 8H), 7.26 (d, J = 9Hz, 2H), 6.40 (s, 2H), 2.97 (s, 12H). ^{13}C NMR (DMSO, 125 MHz):

δ 68.1, 84.8, 98.4, 110.1, 115.0, 115.7, 124.5, 135.7, 142.8, 147.6, 152.7, 153.7. HRMS (EI): m/z calculated for $C_{31}H_{28}IN_5$ [M-I$^-$] = 470.2345; found: 470.2356.

5: dark red crystals, 40 mg, 40%. ^{1}H NMR (DMSO, 500 MHz): δ 8.49 (d, J = 1.8 Hz, 2H), 8.10 (dd, J = 9.1, 1.8 Hz, 2H), 7.54, 7.04 (AA'BB', J = 8.5 Hz, 8H), 7.30 (d, J = 9.1 Hz, 2H), 6.42 (s, 2H), 3.82 (s, 6H). ^{13}C NMR (DMSO, 125 MHz): δ 58.8, 69.2, 85.4, 96.7, 115.1, 116.2, 117.7, 124.6, 136.3, 143.5, 147.9, 153.1, 163.3. HRMS (EI): m/z calculated for $C_{29}H_{22}IN_3O_2$ [M-I$^-$] = 444.1712; found: 444.1714.

Linear optical measurements. Electronic absorption spectra were collected on a UV-VIS absorption spectrometer Lambda 35 (Perkin Elmer, Rodgau, Germany). The spectra were corrected with solvent absorption spectra. Steady-state fluorescence emission spectra were collected on an FLS920-stm spectrometer (Edinburgh Instruments, Livingstone, United Kingdom). The spectra were corrected for the detector response. Fluorescence decays were also acquired on the FLS920-stm spectrometer using Time Correlated Single Photon Counting (TCSPC) technique with a sub-nanosecond pulsed LED (EPLED 320) as an excitation source. Fluorescence decay times were determined from the decays using the least squares fitting method. The fitting was assumed to be correct when the goodness-of-fit value χ^2 was lower than 1.2. Fluorescence quantum yields were measured on a C9920-02G absolute QY measurement system from Hamamatsu (Hamamatsu Photonics Deutschland GmbH, Herrsching am Ammersee, Germany). All measurements were executed using 3ml quartz cuvette (Hellma GmbH, Jena, Germany) with 1 cm light path. All measurements were executed for samples with OD below 0.15.

Two-photon absorption measurements

The two-photon absorption (2PA) measurements were carried out using an FLS9020 fluorescence spectrometer (Edinburgh Instruments Ltd., Livingston, UK) equipped with a R928P photomultiplier (Hamamatsu, Japan) to detect optical signal. Samples were measured in 1.0x1.0 cm quartz cuvettes in a 90° setup with direct excitation from a femtosecond (<100 fs) titan-sapphire-laser (Tsunami HP, Spectra Physics, Santa Clara, CA, USA) with 80 MHz repetition rate. The measurements were carried out in the wavelength range from 700 nm to 900 nm. The pulse spectrum (FWHM 10 nm) was monitored throughout the measurements by a computer-controlled Avaspec-spectrometer (Avantes BV, Apeldoorn, NL). In order to focus the laser beam, an achromatic NIR-lens (Thorlabs GmbH, München, Germany) was integrated into the experimental setup along with a neutral density (ND) filter to adjust average laser power (200 mW to 500 mW). The laser power was monitored by an optical power meter right before starting any measurement. Spectral resolution was set to 1 nm, differences in signal intensity were compensated by adjusting the integration times (0.1 s to 2 s). The dye concentrations were varied between $9.0 \cdot 10^{-7}$ M to $1.5 \cdot 10^{-5}$ M, for optimal signal intensities, depending on the dye and solvent used.

Two-photon-excited fluorescence was used to determine the two-photon absorption cross-sections - σ_{2PA} (2PA-CS). Assuming that the fluorescence quantum yield under one- (Φ_1) and two-photon excitation (Φ_2) remains the same, two-photon excitation σ2PA values were determined using following equation [4]:

$$\sigma_{2PA}^{P} = \frac{c^{S} \cdot \Phi^{S}}{c^{P} \cdot \Phi^{P}} \cdot \frac{\int \lambda^{P} d\lambda}{\int \lambda^{S} d\lambda} \cdot \sigma_{2PA}^{S}$$

where σ_{2PA} is two-photon absorption cross-section, c is concentration, Φ is quantum yield and $\int \lambda d\lambda$ corresponds to the field under a photoluminescence spectrum. The letters P and S denote the values determined for probe or standard (fluorescein), respectively. The σ2PA values are given in Goeppert-Mayer (GM) units, where $1GM = 10^{-50}$ cm^4 s/photon.

Theoretical calculations

All calculations were performed with aid of the Gaussian 09 package.[35] Standard methods, DFT B3LYP/6-31G(d,p) and TDDFT B3LYP/6-31G(d,p) were used for the optimization of the molecular structures and calculations of the electronic transitions energies. Effect of the solvent was included in the polarizable-continuum model (PCM) with the use of the default options of this model implemented in the Gaussian.

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35 See the Supporting Information for more details.

TOC graphic

Intramolecular charge transfer dictates linear and non-linear optical properties of D-π-A$^+$-π-D compounds.

Φ = 53%
σ_2 = 4200 GM

λ_{abs} (CH$_2$Cl$_2$) = 482 nm
λ_{abs} (DMSO) = 474 nm
λ_{em} (CH$_2$Cl$_2$) = 525 nm
λ_{em} (DMSO) = 515 nm