CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201200718

Octupolar Merocyanine Dyes: A New Class of Nonlinear Optical Chromophores

Yevgen M. Poronik,[a] Vincent Hugues,[b] Mireille Blanchard-Desce,*[b] and Daniel T. Gryko*[a]

Dedicated to Professor Jonathan Lindsey on the occasion of his 55th birthday

Abstract: A set of new octupolar merocyanine chromophores was designed and synthesized. These compounds were prepared from the reaction of 1,3,5-triformyl-2,4,6-trihydroxybenzene with heterocyclic nucleophiles. Octupolar dyes were formed exclusively in their open-dye form. The one- and two-photon-absorption spectra of the dyes consist of two bands: The long-wavelength band in the two-photon absorption spectrum (a few hundreds GM above 1000 nm) matches well with the intense, long-wavelength-absorption band that is located in the visible region in the linear spectrum. Interestingly, an additional, much-more-intense TPA band in the NIR region is observed at higher energy, which corresponds to a weakly allowed one-photon electronic transition. Changing the peripheral heterocyclic moieties allows tuning of the optical properties to approach the cyanine limit (i.e., polymethine state), thus resulting in a red-shift of the low-energy one-photon-absorption band as well as to the rise of an intense two-photon-absorption band in the NIR region. To the best of our knowledge, this is the first synthesis and TPA characterization of octupolar merocyanine chromophores with typical low-bond-length alternation.

Keywords: dyes · fluorescence · imaging agents · solvatochromism · two-photon absorption

Introduction

The design of new chromophores that possess nonlinear optical (NLO) properties, such as two-photon absorption (2PA), has been attracting considerable attention in recent years owing to the prospect of using them in a wide range of applications, including the two-photon excited fluorescence (TPEF) microscopy of biological structures,[1,2] 3D data storage,[3] photodynamic therapy,[4] optical limiting,[5] 3D microfabrication,[1a,5f,6] etc. On the other hand, classical one-photon-absorption (1PA) chromophores, such as cyanine and rhodamine dyes, which are very popular in fluorescence microscopy techniques, usually have relatively low two-photon-absorption cross-sections (σ_2) in the spectroscopic range of interest for biological imaging (700–1000 nm); therefore, they require high excitation intensity and/or high concentrations when used as fluorochromes in the multiphoton imaging of biological systems. To lower the excitation intensity (for reduced damage) or scan more rapidly (for dynamic imaging) for the detection of species that have very low concentrations, it is necessary to design fluorescent labels and probes that have much-larger two-photon brightness ($\sigma_2\Phi$, where Φ is the fluorescence quantum yield) than classical fluorescent probes (typically thousands of GM). Whereas fluorophores that have very large two-photon brightness in the red-NIR range also have very large one-photon brightness in the near UV/Vis region,[7,8] the opposite is not true. Indeed, 2PA chromophores belong to very unique class of functional dyes that have some structural peculiarities that are different from usual chromophore systems.[1,9] It has become clear that, for the two-photon technology to realize its full potential, the development of more two-photon-active chromophores that also possess other useful optical or chemical properties, such as high fluorescence quantum yields, easy processability, good photostability, and durability will play a vital role.

There are some principles in the construction of NLO chromophores, which are imposed by the selection rules for 2PA, unlike for 1PA, that result in the particular structure of 2PA systems.[1,9] Large two-photon-absorption cross-sections have often been associated with the extent of conjugation (effective π-delocalization), which leads to an extended charge-separation (a large π-conjugated system). Adding an electron donor (D) and acceptor (A) onto the ends of a conjugated chromophore to give a D-π-A system enhances the transition dipole moment as a consequence of the increase in the displacement of charge during the transition from HOMO to LUMO.

Compared to dipolar systems, centrosymmetric dyes (D-π-A-π-D or A-π-D-π-A) tend to have larger TPA respons-

---

[a] Dr. Y. M. Poronik, Prof. Dr. D. T. Gryko
Institute of Organic Chemistry of the
Polish Academy of Sciences
44/52 Kasprzaka Str., 01-224 Warsaw (Poland)
E-mail: dtgryko@icho.edu.pl

[b] V. Hugues, Dr. M. Blanchard-Desce
Université de Bordeaux, ISM (UMR5255 CNRS)
33400, Bordeaux (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201200718.

es,[1,7] partly because the transition moment in a D-π-A-π-D system is larger than those for the corresponding D-π-A unit, because D-π-A-π-D will be effectively polarized by both parts of the optical field cycle, whereas D-π-A is easily polarized in just one direction. Similarly, centrosymmetric octupolar dyes that are typically built from the branching of several dipolar chromophores through a common donor or acceptor core (i.e., $D(-\pi-A)_3$ or $A(-\pi-D)_3$) can lead to much-larger TPA[10] responses than their dipolar counterpart.

From the point of view of electronic structure, a number of 2PA chromophores belong to a family of push–pull polyenes (structure A, Figure 1) that contain an electron donor and an electron acceptor grafted onto opposite ends of the conjugated system. The contribution of the mesomeric form with charge separation (zwitterionic form) is usually very low and such polyenes have high bond-length alternation (BLA) and moderate charge separation (and polarization) in the ground state.[1,10] The electronic spectra of polyenes are characterized by broad, low- or moderately intense absorption bands. Merocyanine dyes[11] (structure B, Figure 1), although formally similar to polyenes, are completely different from an electronic point of view and belong to a family of polymethine dyes. Indeed, merocyanine dyes contain an odd number of π-centers within the conjugated system, whereas polyenes contain an even number of π-centers.

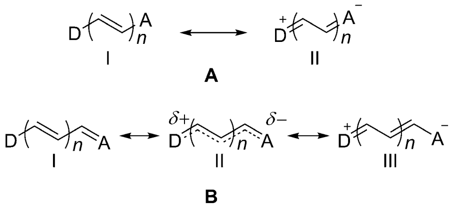


Figure 1. Resonance forms for the polyene (A) and merocyanine chromophores (B).

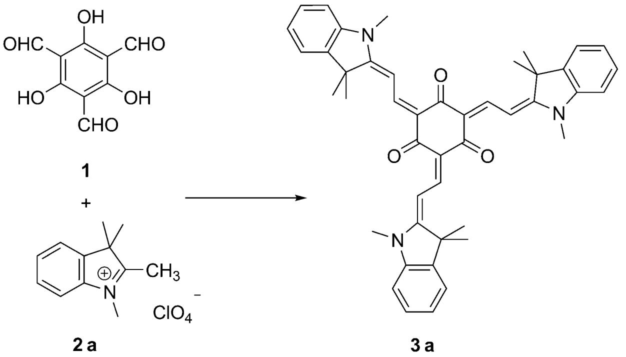
The structure of merocyanine dyes is the superposition of two mesomeric forms: neutral (I) and zwitterionic (III, Figure 1). The relative contribution of these forms depends on the strength of the donor and the acceptor and on the polarity of the solvent. When the two resonance forms contribute equally to the ground-state structure, the molecule exhibits essentially no BLA (the so-called “cyanine limit”, that is, state II). In their electronic spectra, merocyanine dyes are characterized by intense and sharp cyanine-like absorption bands. Compared to polyene molecules, merocyanine dyes may have more-efficient intramolecular charge-transfer (ICT) between the donor and the acceptor and, hence, a higher dipole moment (or polarization) in the ground state, as well as a larger 2PA cross-section for a shorter conjugated chain.[12] Overall, only a few papers on the study of 2PA of merocyanine dyes have been published.[13–15]

Abstract in Polish: *Otrzymano barwniki funkcjonalne typu merocyjanin o budowie oktupolowej. Synteza oparta jest o reakcję 1,3,5-triformylo-2,4,6-trihydroksybenzenu z nukleofilami heterocyklicznymi. Udowodniono, że barwniki istnieją wyłącznie w formie otwartej. Otrzymane związki absorbują silnie światło czerwone i pomarańczowe, wykazują fluorescencję ($\lambda_{em}=590$–690 nm) oraz dwa silne pasma w absorpcji dwufotonowej ($\sigma_2=500$–2300 GM). Zmiana jednostki heterocyklicznej pozwala na modulowanie właściwości optycznych i zbliżenie się do tzw. granicy cyjaninowej, co bezpośrednio skutkuje batochromowym przesunięciem maksimum absorpcji jednofotonowej i zwiększeniem intensywności absorpcji dwufotonowej.*

This paper addresses the synthesis and investigation of new octupolar conjugated merocyanine dyes as a combination of three dipolar merocyanines in one system. To the best of our knowledge, no such octupolar merocyanines have been reported previously.

Results and Discussion

To obtain the desired merocyanines, phloroglucinol trialdehyde (**1**)[16] was chosen as the building block. The reactivity of the aldehyde groups was high enough to undergo condensation with three equivalents of quaternary heterocyclic salts. The reaction between trialdehyde **1** and methylindolium salt **2a** in boiling pyridine gave octupolar merocyanine **3a** (Scheme 1).



Scheme 1. Reagents and conditions: pyridine (Py), reflux, 10 min; yield: 59 %.

The generic dipolar merocyanine structure commonly exists in the form of isomeric spiropyran **I** (Figure 2) in which the conjugation chain is broken. Spiropyran **I** can undergo reversible isomerization to form merocyanine **II** under UV irradiation.[17a,b]

The ^{1}H NMR spectrum of compound **3a** reveals six signals in the aromatic region (see the Supporting Information); moreover, the absorption spectrum in solution shows an intense and sharp absorption band at around 570 nm, which suggests a symmetrical cyanine-type electronic structure. According to the ^{1}H NMR spectrum, no isomerization occurred in the solution of compound **3a** after several days.

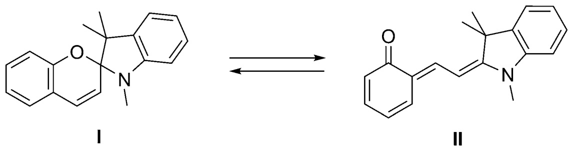


Figure 2. Tautomerism between the spiropyran and merocyanine forms.

Dye **3a** was also synthesized in high yield under standard conditions (boiling EtOH) by using Fischer's base (**2a**)[17c] and no spiropyran derivative was detected.

Compound **3a** belongs to a class of merocyanine dyes with an octupolar structure that, until now, has no reported analogues in the literature. This fact requires the additional consideration of the electronic structure of this dye. The structure of such octupolar chromophores can be depicted in four limiting forms (Figure 3): one neutral (**N**) and three mesoionic forms in which one dipole arm possesses zwitterionic character (**Z1**–**Z3**)[18] and where the negative charge is delocalized between the oxygen atoms of the central electron-acceptor framework. However, the energy of the limiting forms that contain multiple charge-transferred dipole arms is too high; therefore, these latter forms do not make any significant contribution. As the result of the superposition of these forms, the electron density is partly shifted from the end moieties towards the central part of molecule.

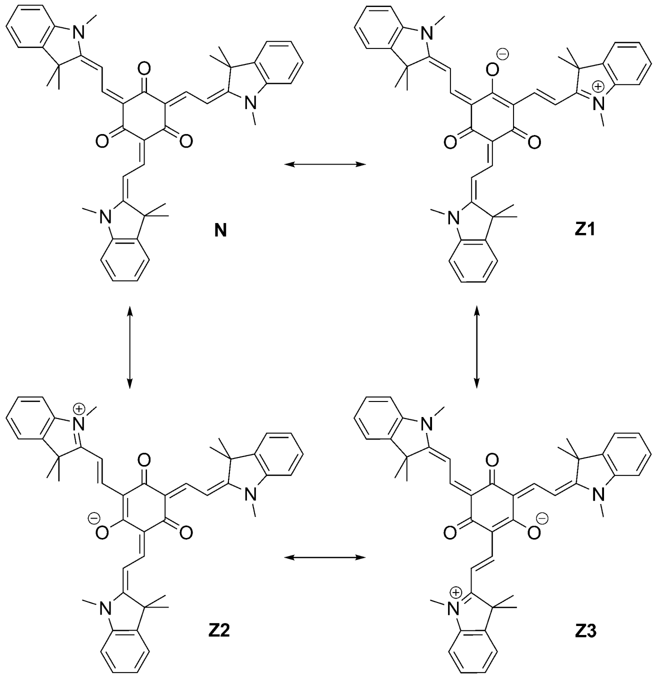
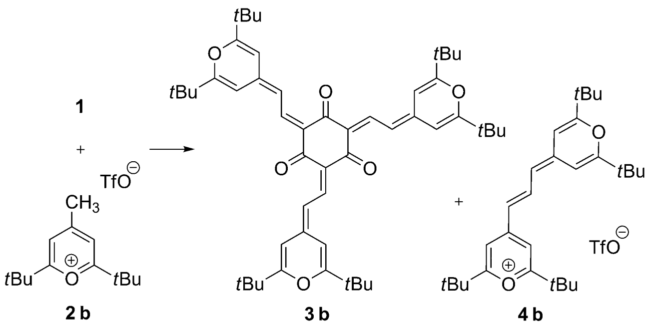


Figure 3. Limiting forms for octupolar merocyanine **3a** that was derived from a phloroglucinol core.

For a better understanding of the nature of this chromophore, we attempted to obtain analogous dyes that contain peripheral end-groups with lower and higher electron-donor ability. It appeared that the reaction between methylpyrylium salt **2b** and aldehyde **1** in pyridine at room temperature, instead of desired dye **3b**, gave rise to pyrylocyanine triflate **4b** as a major product, accompanied by traces of merocyanine **3b** (Scheme 2). Subsequently, we found that this reaction should be performed in two steps: 1) heating in boiling EtOH in the absence of base and 2) the subsequent addition of triethylamine afforded the desired merocyanine (**3b**), which was isolated as the major product (Scheme 2).



Scheme 2. Reagents and conditions: a) Py, RT, 12 h; yield: **3b**: 5 %, **4b**: 77 %. b) (i) EtOH, reflux, 15 min; (ii) addition of NEt$_3$, reflux, 10 min; yield: **3b**: 27 %, **4b**: traces.

Interestingly, in this case, the contribution of the various zwitterionic forms in the description of the electronic structure is expected to be higher because aromaticity is also gained in both the electron-donating peripheral moieties and in the central ring upon charge separation. Based on a simplified four-essential-state model, getting closer to the cyanine limit should lead to both a red-shift in the 1PA response and a marked increase in the 2PA responses for such octupolar systems.[19] Because charge separation (and charge multiplication) costs energy, in most situations, the neutral form dominates in the ground state. This situation is, in particular, the case for the recently reported 2PA-active octupolar derivatives, which were all built from either a typical donor[7d,m] or acceptor aromatic core.[7i,10a] The octupolar merocyanines investigated herein do not contain such an aromatic core. This property gives more chance to shift the electronic structure towards the cyanine limit and, possibly, overpass it by increasing the donor strength of the peripheral moieties.

Following this line, other peripheral moieties that confer aromaticity upon charge separation were investigated to tune the contribution of the zwitterionic forms in the ground state and to probe the resulting optical properties. Trialdehyde **1** readily reacted with 2,3-dimethylbenzothiazolium and 1,2-dimethylquinolinium salts to form the desired merocyanines **3c** and **3d**, respectively (Figure 4). However, these latter dyes seemed to be insoluble in most organic solvents, thus making it impossible to obtain analytical pure samples.

To overcome this obstacle, trialdehyde **1** was condensed with benzothiazolium and quinolinium salts, which contained longer *N*-alkyl groups (**2e** and **2f**, respectively). This approach allowed us to obtain isoelectronic analogues of dyes **3c** and **3d** (**3e** and **3f**, respectively, Scheme 3).

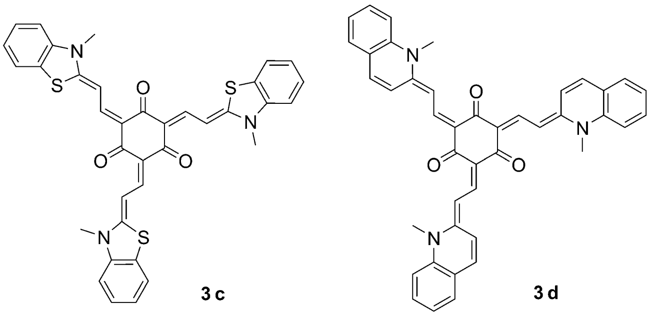
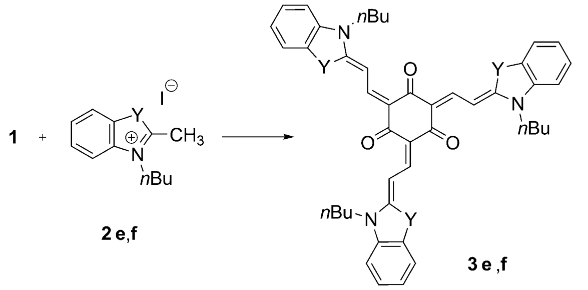


Figure 4. Structures of compounds **3c** and **3d**.



Scheme 3. Reagents and conditions: Py, reflux. **e**: Y = S, yield: 14 %; **f**: Y = CH=CH, yield: 50 %.

Only a few dye molecules with some similarity to merocyanines **3a**–**3f** are known in the literature. The tetraone derivative[15] is a quadrupolar analogue of octupolar dyes **3a**–**3f**. Analogously, it contains a central electron acceptor moiety that is conjugated with two electron-donating peripheral heterocycles. The major difference between octupolar merocyanines **3a**–**3f** and tetraone is that tetraone contains two chromophores that are formally non-conjugated with each other, that is, the zwitterionic forms do not result in extended π-conjugated systems, as is the case here. Tetraone shows a 1PA absorption maximum at 624 nm and its 2PA spectrum consists of a broad band that overlaps the whole 700–1150 nm spectroscopic range with $\sigma_2^{max} \approx 2700$ GM at 820 nm.

Ketocyanines[20] can also be considered as analogues of octupolar merocyanines **3a**–**3f**. Their structure can also be considered to be quadrupolar with the carbonyl group as an electron acceptor. In the case of these dyes, two chromophore arms are conjugated in one π-system (via the intermediate zwitterionic form). Ketocyanines are sensitive to the pH value and, in acidic media, they are reversibly protonated, thus switching to a carbocyanine form. Ketocyanines exhibit moderate linear absorption in the spectroscopic range 550–650 nm and show large quadratic hyperpolarizabilities.[20d]

Linear optical properties: The synthesized octupolar merocyanine dyes display two absorption bands in the visible region: an intense band at long-wavelength with a well-resolved vibrational structure and a much-weaker band at shorter wavelength (Figure 5, Table 1).

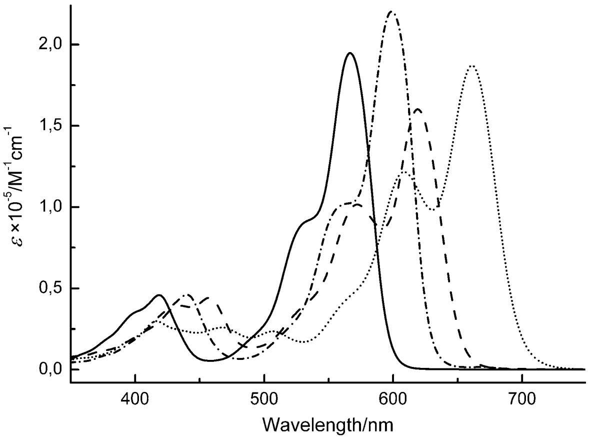


Figure 5. Absorption spectra of octupolar merocyanine dyes **3a** (solid line), **3b** (dashed line), **3e** (dashed dotted line), and **3f** (dotted line) in toluene.

Table 1. Linear optical properties of the synthesized dyes.

Compound	λ_{abs}^{max} [nm]	$\varepsilon_{max} \times 10^{-3}$ [$M^{-1}cm^{-1}$]	FWHM [cm^{-1}]	λ_{em}^{max} [nm]	Stokes shift [cm^{-1}]	Φ [%]
3a (toluene)	567	195	1356	596	858	3.4
	419	45.8				
3a (THF)	562	141	2026	598	1070	6.7
	418.5	36.5				
3b (toluene)	619	160	2272	648	723	0.91
	457	44.2				
3b (THF)	615	152	2524	655	990	1.9
	571.5	105				
	456.5	46.0				
3e (toluene)	599	220	1184	627	745	17.2
	440	46.0				
3e ($CHCl_3$)	602.5	215	1432	627	750	12.3
	451.5	45.3				
3f (toluene)	661	187	2172	690	636	0.62
	506	24.0				
3f ($CHCl_3$)	659.5	213	2194	685	550	0.28
	609.5	128				
	511.5	31.2				

When comparing the linear absorptions of dyes **3a**–**3f**, some similarities can be found. Because the synthesized dyes consist of end moieties that possess different donor–acceptor properties, the electron densities in the structures of the merocyanines is distributed in different ways. Let us analyze the influence of the solvent on the shape of the absorption bands. According to the Franck–Condon principle, the smaller BLA in the polymethine chain in the ground state, the smaller the change in the bond lengths in the excited state. Consequently, the absorption spectra of such electron-symmetrical dyes should exhibit strong 0–0 transitions at the expense of the vibronic transitions.[21]

The absorption spectrum of the octupolar merocyanine that contains the weakest electron-donating peripheral moieties (**3b**) displays a relatively broad, long-wavelength absorption band with well-resolved vibronic structure in low-polarity solvents. The value of the band width at half maximum (FWHM) is relatively high (Table 1). In addition, increasing the solvent polarity gives rise to a definite red-shift and broadening of the low-energy absorption band (Figure 6), as well as an increase in Stokes shift, whereas the intensity ratio of the 0–1 sub-band relative to that of the 0–0 sub-band (I_{0-1}/I_{0-0}) is not much affected (0.66 in 1,4-dioxane). From this variation, we can speculate that the electronic structure of merocyanine **3b** is characterized by a dominant contribution of the neutral form in the ground state (i.e., $\rho < 0.5$ in a four-essential-state model).[19]

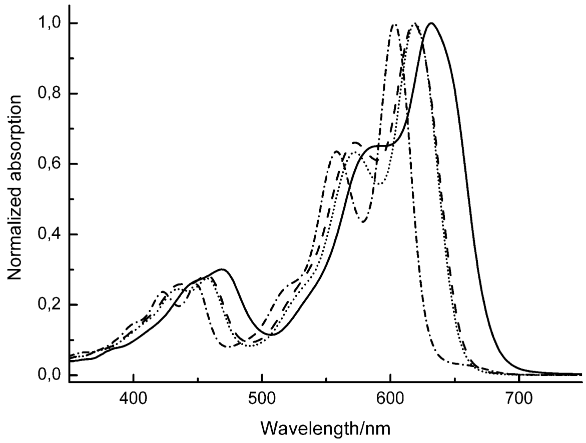


Figure 6. Normalized absorption spectra of merocyanine **3b** in DMSO (solid line), toluene (dotted line), 1,4-dioxane (dashed line), and cyclohexane (dashed dotted line).

Merocyanine **3a** contains peripheral heterocyclic moieties with increased electron-donating ability compared to dye **3b**. The absorption spectra of merocyanine **3a** exhibits somewhat narrower absorption bands at long-wavelength and its FWHM is smaller than that of merocyanine **3b.** In addition, increasing the solvent polarity gives rise to a definite red-shift of the low-energy absorption band, whilst the I_{0-1}/I_{0-0} ratio decreases (Figure 7).

The fine vibronic structure is only resolved in cyclohexane solution (with a corresponding intensity ratio of $I_{0-1}/I_{0-0} = 0.57$). This result suggests that the electronic structure of merocyanine **3a** in nonpolar solvents is characterized by a dominant neutral form but get closer to the cyanine limit (or polymethine state) in polar solvents (i.e., $\rho \leq 0.5$ in the four-essential-state model).[19]

Further increasing the electron-donating ability of the peripheral heterocyclic moieties (dye **3e**) gives rise to symmetrization of the π-system of the merocyanines. In their electronic spectra, dye **3e** exhibits a narrow absorption band at long-wavelength with a minimal FWHM among other octupolar merocyanines (Table 1). Dye **3e** demonstrates the strongest linear absorption among the other octupoles and its absorption hardly depends on the polarity of the solvent. The intensity ratio ($I_{0-1}/I_{0-0} = 0.43$ in cyclohexane) is the smallest within the series (Figure 8). Evidently, the electronic structure of dye **3e** approaches the cyanine limit (i.e., $\rho \approx 0.5$ in the four-essential-state model).[19]

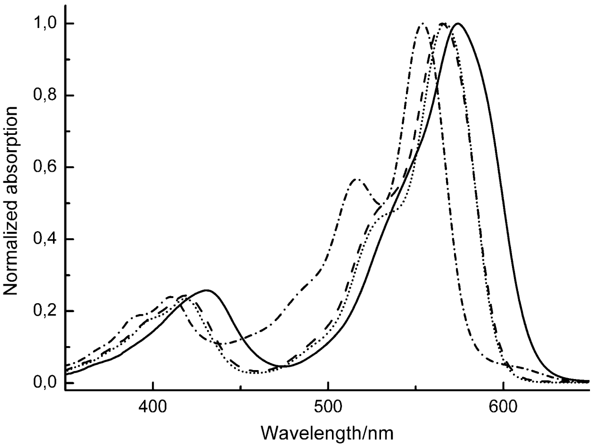


Figure 7. Normalized absorption spectra of merocyanine **3a** in DMSO (solid line), toluene (dotted line), 1,4-dioxane (dashed line), and cyclohexane (dashed dotted line).

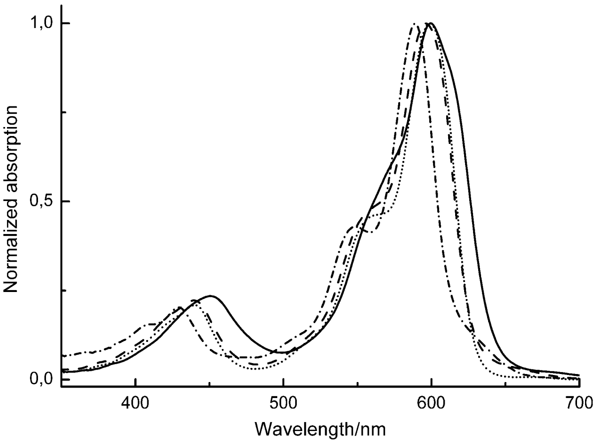


Figure 8. Normalized absorption spectra of merocyanine **3e** in DMSO (solid line), toluene (dotted line), 1,4-dioxane (dashed line), and cyclohexane (dashed dotted line).

This electronic structure also results in the smallest Stokes shift and the largest fluorescent quantum yield among the other dyes in the series. This result is corroborated by the value of the coupling constant (*J*) between the vicinal vinylic protons in the C−C bond that connects the phloroglucinol core and the peripheral moieties in the case of merocyanine **3e**. Indeed, the *J* values ($CDCl_3$) are intermediate between the coupling constants of the vicinal vinylic protons through a C−C single bond (10 Hz, (anticoplanar geometry, as in the neutral form) or through a C=C double bond (16 Hz, *trans* geometry, as in the zwitterionic forms).

Merocyanine **3f** contains peripheral heterocyclic moieties that have the strongest electron-donating character. The absorption spectrum of dye **3f** display a well-resolved vibronic structure and the intensity ratio ($I_{0-1}/I_{0-0} = 0.73$, in cyclohexane) is the highest within the series (Figure 9). This latter result indicates some degree of BLA in the ground state of merocyanine **3f**, which is corroborated by the larger FWHM value compared to octupolar merocyanine **3e** (similar to

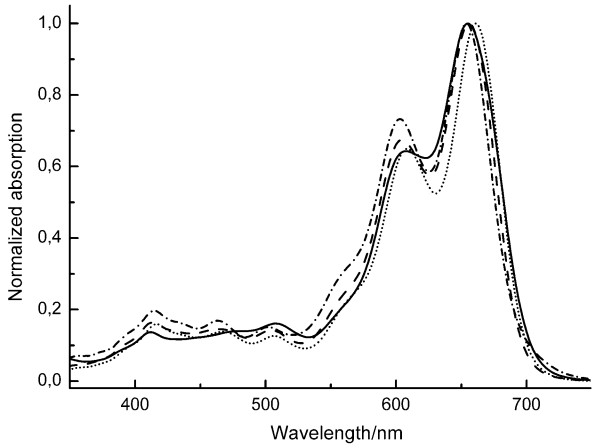


Figure 9. Normalized absorption spectra of merocyanine **3f** in DMSO (solid line), toluene (dotted line), 1,4-dioxane (dashed line), and cyclohexane (dashed dotted line).

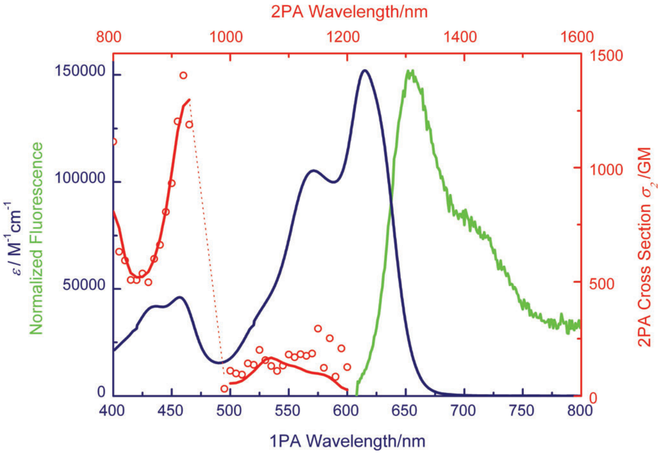


Figure 11. Linear absorption (blue), fluorescence (green) and two-photon absorption spectra (red) of merocyanine **3b**.

that of dye **3b**). Increasing the solvent polarity does not significantly affect the position of the absorption band but rather induces a decrease in the I_{0-1}/I_{0-0} ratio and in the Stokes shift.

Consequently, in the case of dye **3f**, we speculate that the contribution of the limiting forms that have zwitterionic character is higher than that of the neutral form (i.e., $\rho \geq 0.5$ in the four-essential-state model).[19]

Nonlinear optical properties: There are some parallels between the 1PA and 2PA of merocyanines within the series. For better comparison, the 2PA spectra are shown on the same graph as the 1PA spectra, with separate axes, by multiplying the wavelength scale by 2 (Figure 10 and Figure 11). The linear absorption spectra of dyes **3a**–**3f** consist of two bands: an intense, long-wavelength band and a weaker, short-wavelength band. At the same time, the 2PA spectra of the octupolar merocyanines display low-intensity long-wavelength maxima (150–200 GM) that match well with the $S_0 \rightarrow S_1$ transition (two-photon allowed for octupolar chromophores),[7c] which is typical of polymethine dyes. Conversely, the 2PA spectra of octupolar merocyanines also display high-intensity, short-wavelength 2PA bands that match well with the short-wavelength absorption band in the linear electronic spectra and are most-probably related to the one-photon forbidden transition in C_3 molecules (and the two-photon allowed electronic transition $S_0 \rightarrow S_2$). Here, this transition becomes partially 1PA allowed owing to relaxation of the molecular geometry to a conformation with a lower symmetry.[7c]

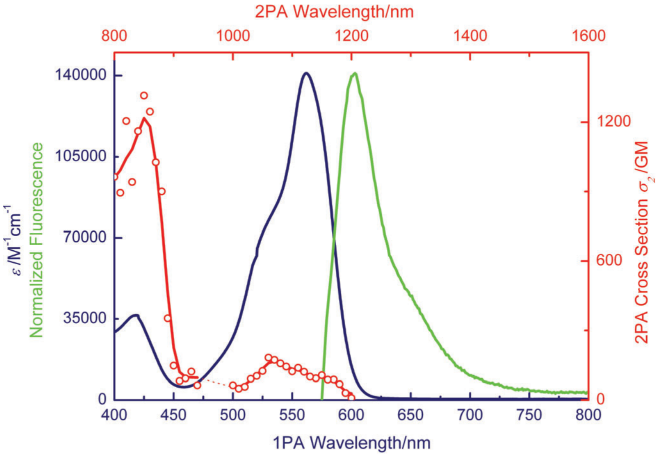


Figure 10. Linear absorption (blue), emission (green), and two-photon absorption spectra (red) of merocyanine **3a**.

For merocyanines **3a** and **3b**, which have the weakest electron-donating heterocyclic moieties, the maximum 2PA cross-sections in the NIR region are comparable: $\sigma_2^{\max} \approx 1300$ GM (Table 2). In the case of merocyanine **3e**, the linear absorption band is close to the higher-energy 2PA band, thereby making it difficult to reach the maxima value by using TPEF experimental methods. This result is consistent with merocyanine **3e**, which is very close to the cyanine limit (or the ideal polymethine state), where 2PA become 1PA resonant, thereby giving rise to giant 2PA responses.[19]

Table 2. Two-photon absorption of octupolar merocyanines.

Compound	$2\lambda_{OPA}^{\max}$ [nm]	$\lambda_{TPA}^{\max1}$ [nm]	$\sigma_2^{\max1}$ [GM]	$\lambda_{TPA}^{\max2}$ [nm]	$\sigma_2^{\max2}$ [GM]
3a (THF)	1124	1150	98	850	1315
		1110	129		
		1070	167		
3b (THF)	1230	1200	162	930	1293
		1150	214		
		1050	166		
3e ($CHCl_3$)	1205	>1200	–	<860	>485[a]
3f ($CHCl_3$)	1319	>1200	–	890	2274

[a] The 1PA transition is close to the wavelength of the 2PA laser, making it difficult to resolve the 2PA band.

On the other hand, merocyanine **3f** contains the strongest electron-donating peripheral heterocyclic moieties and, consequently, has the strongest charge separation in the ground state with the largest 2PA response ($\sigma_2^{\max} = 2300$ GM).

Conclusions

A number of new octupolar merocyanine dyes were designed and synthesized. These molecules consist of three merocyanine chromophores that are conjugated in one π-system to form octupolar frameworks with a central electron-withdrawing fragment and peripheral electron-donor moieties. Their main unique structural feature comes from the nature of the (acceptor) core, which gains some aromatic character upon charge-separation. As a result, it becomes possible to modulate the relative contributions of the neutral (polyene like) and zwitterionic forms (charge-separated) by using peripheral heterocyclic donors of various strengths and investigate derivatives in the same series on both side of the cyanine limit. In addition, this procedure allowed us to obtain octupolar structures that have electronic structures that are close to the cyanine limit, in which the higher-energy 2PA band (close to 1PA resonance) is expected to be extremely intense.

The linear absorption spectra of the dyes consist of two bands: an intense, long-wavelength band and a weak, short-wavelength band. The two-photon-absorption spectra also display two maxima. The low-intensity, long-wavelength band corresponds to a two-photon allowed transition for octupolar chromophores ($S_0 \rightarrow S_1$) and matches well with the long-wavelength absorption band in the linear spectrum. The intense higher-energy 2PA band matches well with the short-wavelength absorption band in the linear electronic spectra, which corresponds to a one-photon forbidden electronic transition ($S_0 \rightarrow S_2$).

Analysis of the linear absorption spectra suggests that, whilst the merocyanine that contains peripheral pyrylium moieties possesses partial polyene character, the structure of the dye that contains peripheral benzothiazole moieties is close to the “polymethine state”. Moreover, the merocyanine that contains peripheral quinoline moieties exists mainly in a form in which the charges are partially separated; this form results in the largest 2PA cross-section in the NIR range among the other dyes investigated.

Experimental Section

All chemicals were used as received unless otherwise noted. Reagent-grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All of the reported ^{1}H NMR spectra were collected on 400 MHz or 500 MHz spectrometers. Chemical shifts (δ, ppm) were determined by using TMS as an internal reference; *J* values are given in Hz. Column chromatography was either performed on silica gel (200–400 mesh) or on neutral aluminum oxide (70–230 mesh). Mass spectra were obtained by field-desorption MS (FDMS). Quaternary heterocyclic salts were prepared according to the following literature procedures: **2b**,[22] **2e**,[23] and **2f**.[24]

(2*E*,4*E*,6*E*)-2,4,6-tris((*E*)-2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)-cyclohexane-1,3,5-trione (3a): Trialdehyde **1** (105 mg, 0.5 mmol) and indolinium salt **2a** (450 mg, 1.65 mmol) were heated at reflux in pyridine (4 mL) for 10 min. After cooling, pyridine was evaporated and the crude product was eluted through silica gel (CH_2Cl_2/CH_3OH, 95:5). The solvent was evaporated and the product was purified for a second time by column chromatography on silica gel (CH_2Cl_2/Et_2O, 3:1). After evaporating the eluent, the product was dried to give 200 mg (59 %) of merocyanine **3a**. M.p.: 238 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 8.70$ (d, $^3J(\mathrm{H,H}) = 11$ Hz, 3H; *CH*), 7.91 (d, $^3J(\mathrm{H,H}) = 14$ Hz, 3H *CH*), 7.36–7.31 (m, 6H; Ar*H*), 7.12 (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3H; Ar*H*), 6.98 (d, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3H; Ar*H*), 3.54 (s, 9H; NCH_3), 1.78 ppm (s, 18H; C(CH_3)$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 173.6$, 146.8, 143.7, 140.8, 127.9, 122.8, 121.8, 108.6, 98.9, 48.0, 30.4, 28.8 ppm; UV/Vis (toluene): $\lambda_{\max}(\varepsilon) = 567$ (195 000), 419 nm (46 000 $\mathrm{mol^{-1}\,m^3\,cm^{-1}}$); HRMS (FD): *m*/*z* calcd for $C_{45}H_{45}N_3O_3$: 675.3461 $[M]^+$; found: 675.3486.

(2*E*,4*E*,6*E*)-2,4,6-tris(2-(2,6-di-tert-butyl-4*H*-pyran-4-ylidene)ethylidene)-cyclohexane-1,3,5-trione (3b): Trialdehyde **1** (105 mg, 0.5 mmol) and pyrylium salt **2b** (550 mg, 1.55 mmol) were heated at reflux in EtOH (5 mL) for 15 min. After cooling, triethylamine (200 mg, 2 mmol) was added and the reaction was heated at reflux for an additional 10 min. The solvent was evaporated and cyclohexane (20 mL) was added to the residue. The product was dissolved, the solid material was filtered off, and cyclohexane was evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O, 9:1). After evaporating the eluent, the product was dried to give 110 mg (27 %) of merocyanine **3b**. M.p.: 322 °C (dec.); ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 8.45$ (br s, 3H; *CH*), 7.70 (d, $^3J(\mathrm{H,H}) = 13.5$ Hz, 3H; *CH*), 6.90 (s, 3H; Ar*H*), 6.33 (s, 3H; Ar*H*), 1.34 (s, 27H; C(CH_3)$_3$), 1.29 ppm (s, 27H; C(CH_3)$_3$); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 185.4$, 169.5, 150.8, 144.0, 122.7, 113.1, 108.7, 101.3, 36.4, 36.1, 27.7, 27.6 ppm; UV/Vis (toluene): $\lambda_{\max}$ (ε) = 619 (160 000), 572 (102 000), 457 (44 000), 435 nm (39 000 $\mathrm{mol^{-1}\,m^3\,cm^{-1}}$); HRMS (FD) *m*/*z* calcd for $C_{51}H_{66}O_6$: 774.4859 $[M]^+$; found: 774.4843; elemental analysis calcd (%) for $C_{51}H_{66}O_6$: C 79.03, H 8.58; found: C 78.81, H 8.55.

General procedure for preparation of dyes 3e and 3f: Trialdehyde **1** (105 mg, 0.5 mmol), the heterocyclic salt (1.65 mmol), and piperidine (250 mg, 3 mmol) were heated at reflux in pyridine (4 mL) for 5 min. After cooling, the reaction was diluted with Et_2O (30–40 mL).

(2*E*,4*E*,6*E*)-2,4,6-tris((*Z*)-2-(3-butylbenzo[d]thiazol-2(3H)-ylidene)ethylidene)cyclohexane-1,3,5-trione (3e): The product was filtered and the crude product was eluted through silica gel (CH_2Cl_2/CH_3OH 95:5). The solvent was evaporated and the residue was recrystallized from toluene to give 90 mg (14 %) of merocyanine **3e**. M.p.: 178 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.43$ (d, $^3J(\mathrm{H,H}) = 12.5$ Hz, 3H, -*CH*=), 8.13 (d, $^3J(\mathrm{H,H}) = 13$ Hz, 3H, -*CH*=), 7.52 (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H, ArH), 7.33 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H, ArH), 7.18 (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3H, ArH), 7.12 (d, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H, ArH), 4.16 (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 6H, NCH_2), 1.89 (quintet, $^3J(\mathrm{H,H}) = 7.5$ Hz, 6H, CH_2), 1.55 (sextet, $^3J(\mathrm{H,H}) = 7.5$ Hz, 6H, CH_2), 1.05 ppm (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.8$, 146.1, 141.9, 126.9, 126.0, 123.5, 122.1, 111.0, 97.8, 46.0, 29.2, 20.3, 13.8 ppm; UV/Vis (toluene): $\lambda_{\max}$ (ε) = 599 (220 000), 440 nm (46 000 $\mathrm{mol^{-1}\,m^3\,cm^{-1}}$); HRMS (FD) *m*/*z* calcd for $C_{45}H_{45}N_3O_3S_3$: 771.2623 $[M^+]$; found: 771.2628.

(2*E*,4*E*,6*E*)-2,4,6-tris((*E*)-2-(1-butylquinolin-2(1H)-ylidene)ethylidene)cyclohexane-1,3,5-trione (3f): The solvents were decanted and the oily material was washed several times with Et_2O. The product was purified by column chromatography on aluminum oxide (CH_2Cl_2/CH_3OH, 98:2) to give 190 mg (50 %) of merocyanine **3f**. M.p.: 183 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.78$ (br s, 3H; *CH*), 8.29 (d, $^3J(\mathrm{H,H}) = 13.5$ Hz, 3H; *CH*), 7.93 (d, $^3J(\mathrm{H,H}) = 9.5$ Hz, 3H; Ar*H*), 7.51 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H; Ar*H*), 7.46 (d, $^3J(\mathrm{H,H}) = 7.5$ Hz, 3H; Ar*H*), 7.38–7.32 (m, 6H; 2× Ar*H*), 7.20 (t, $^3J(\mathrm{H,H}) = 8.0$ Hz, 3H; Ar*H*), 4.23 (br s, 6H; NCH_2), 1.96 (br s, 6H; CH_2), 1.72 (sextet, $^3J(\mathrm{H,H}) = 7.5$ Hz, 6H; CH_2), 1.13 ppm (t, $^3J(\mathrm{H,H}) = 7.5$ Hz, 9H; CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 185.6, 153.7, 145.1, 140.0, 132.3, 131.0, 128.6, 124.5, 123.1, 120.4, 114.4, 102.6, 47.3, 28.4, 20.3, 14.0 ppm; UV/Vis (toluene): $\lambda_{\max}$ (ε) = 661 (187 000), 608 (122 000), 507 (24 000), 467 (26 000), 416 nm (30 000 $\mathrm{mol^{-1}\,m^3\,cm^{-1}}$); HRMS (FD): *m*/*z* (%) calcd for $C_{51}H_{51}N_3O_3$: 753.3930 $[M]^+$; found: 753.3928.

Acknowledgements

This work was funded by the Foundation for Polish Science (TEAM-2009-4/3). M.B.D. thanks the Conseil Regional d'Aquitaine for financial support (Chaire d'excellence grant).

[1] For a recent review, see: a) M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem.* **2009**, *121*, 3292–3316; *Angew. Chem. Int. Ed.* **2009**, *48*, 3244–3266; b) H. M. Kim, B. R. Cho, *Chem. Commun.* **2009**, 153–164; c) H. Meier, *Angew. Chem.* **2005**, *117*, 2536–2561; *Angew. Chem. Int. Ed.* **2005**, *44*, 2482–2506; d) M. Rumi, S. Barlow, J. Wang, J. W. Perry, S. R. Marder, *Adv. Polym. Sci.* **2008**, *213*, 1–95; e) G. S. He, L.-S. Tan, Q. Zheng, P. N. Prasad, *Chem. Rev.* **2008**, *108*, 1245–1330; f) H. M. Kim, B. R. Cho, *Acc. Chem. Res.* **2009**, *42*, 863–872; g) F. Terenziani, C. Katan, E. Badaeva, S. Tretiak, M. Blanchard-Desce, *Adv. Mater.* **2008**, *20*, 4641–4678.

[2] a) S. Yao, H.-Y. Ahn, X. Wang, J. Fu, E. W. Van Stryland, D. J. Hagan, K. D. Belfield, *J. Org. Chem.* **2010**, *75*, 3965–3974; b) C. D. Andrade, C. O. Yanez, L. Rodriguez, K. D. Belfield, *J. Org. Chem.* **2010**, *75*, 3975–3982; c) D. R. Larson, W. R. Zipfel, R. M. Williams, S. W. Clark, M. P. Bruchez, F. W. Wise, W. W. Webb, *Science* **2003**, *300*, 1434–1437; d) L. Ventelon, S. Charier, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Angew. Chem.* **2001**, *113*, 2156–2159; *Angew. Chem. Int. Ed.* **2001**, *40*, 2098–2101; e) T. R. Krishna, M. Parent, M. H. V. Werts, S. Gmouh, A.-M. Caminade, L. Moreaux, S. Charpak, J.-P. Majoral, M. Blanchard-Desce, *Angew. Chem.* **2006**, *118*, 4761–4764; *Angew. Chem. Int. Ed.* **2006**, *45*, 4645–4648.

[3] a) D. A. Parthenopoulos, P. M. Renzepis, *Science* **1989**, *245*, 843–845; b) C. C. Corredor, Z.-L. Huang, K. D. Belfield, A. R. Morales, M. V. Bondar, *Chem. Mater.* **2007**, *19*, 5165–5173.

[4] a) S. Kim, T. Y. Ohulchanskyy, H. E. Pudavar, R. K. Pandey, P. N. Prasad, *J. Am. Chem. Soc.* **2007**, *129*, 2669–2675; b) K. Ogawa, Y. Kobuke, *Org. Biomol. Chem.* **2009**, *7*, 2241–2246; c) C. B. Nielsen, J. Arnbjerg, M. Johnsen, M. Jørgensen, P. R. Ogilby, *J. Org. Chem.* **2009**, *74*, 9094–9104; d) J. R. Starkey, A. K. Rebane, M. A. Drobizhev, F. Q. Meng, A. J. Gong, A. Elliott, K. McInnerney, C. W. Spangler, *Clin. Cancer Res.* **2008**, *14*, 6564–6573; e) H. A. Collins, M. Khurana, E. H. Moriyama, A. Mariampillai, E. Dahlstedt, M. Balaz, M. K. Kuimova, M. Drobizhev, V. X. D. Yang, D. Phillips, A. Rebane, B. C. Wilson, H. L. Anderson, *Nat. Photonics* **2008**, *2*, 420–424; f) M. Gary-Bobo, Y. Mir, C. Rouxel, D. Brevet, I. Basile, M. Maynadier, O. Mongin, M. Blanchard-Desce, A. Morère, M. Garcia, J.-O. Durand, L. Raehm, *Angew. Chem.* **2011**, *123*, 11627–11631; *Angew. Chem. Int. Ed.* **2011**, *50*, 11425–11429.

[5] a) P.-A. Bouit, G. Wetzel, G. Berginc, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonnière, K. Kamada, O. Maury, C. Andraud, *Chem. Mater.* **2007**, *19*, 5325–5335; b) Q. Zheng, G. S. He, P. N. Prasad, *Chem. Phys. Lett.* **2009**, *475*, 250–255; c) G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt, R. McKellar, A. G. Dillard, *Opt. Lett.* **1995**, *20*, 435–437; d) J. E. Ehrlich, X. L. Wu, I. Y. S. Lee, Z. Y. Hu, H. Röckel, S. R. Marder, J. W. Perry, *Opt. Lett.* **1997**, *22*, 1843–1845; e) M. Charlot, N. Izard, O. Mongin, D. Riehl, M. Blanchard-Desce, *Chem. Phys. Lett.* **2006**, *417*, 297–302; f) A. Rebane, M. Drobizhev, N. S. Makarov, B. Koszarna, M. Tasior, D. T. Gryko, *Chem. Phys. Lett.* **2008**, *462*, 246–250; g) G. Lemercier, J.-C. Mulatier, C. Martineau, R. Anémian, C. Andraud, I. Wang, O. Stéphan, N. Amari, P. Baldeck, *C. R. Chim.* **2005**, *8*, 1308–1316.

[6] a) S. Maruo, O. Nakamura, S. Kawata, *Opt. Lett.* **1997**, *22*, 132–134; b) S. Kawata, H.-B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, *412*, 697–698; c) W. Zhou, S. M. Kuebler, K. L. Braun, T. Yu, J. K. Cammack, C. K. Ober, J. W. Perry, S. R. Marder, *Science* **2002**, *296*, 1106–1109; d) F. Claeyssens, E. A. Hasan, A. Gaidukeviciute, D. S. Achilleos, A. Ranella, C. Reinhardt, A. Ovsianikov, X. Shizhou, C. Fotakis, M. Vamvakaki, B. N. Chichkov, M. Farsari, *Langmuir* **2009**, *25*, 3219–3223; e) I. Sakellari, E. Kabouraki, D. Gray, V. Purlys, C. Fotakis, A. Pikulin, N. Bityuryn, M. Vamvakaki, M. Farsari, *ACS Nano* **2012**, *6*, 2302–2311.

[7] a) S.-J. Chung, S. Zheng, T. Odani, L. Beverina, J. Fu, L. A. Padilha, A. Biesso, J. M. Hales, X. Zhan, K. Schmidt, A. Ye, E. Zojer, S. Barlow, D. J. Hagan, E. W. Van Stryland, Y. Yi, Z. Shuai, G. A. Pagani, J.-L. Brédas, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **2006**, *128*, 14444–14445; b) S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S.-J. Jeon, B. R. Cho, *Org. Lett.* **2005**, *7*, 323–326; c) D. Beljonne, W. Wenseleers, E. Zojer, Z. Shuai, H. Vogel, S. J. K. Pond, J. W. Perry, S. R. Marder, J.-L. Brédas, *Adv. Funct. Mater.* **2002**, *12*, 631–641; d) G. Bordeau, R. Lartia, G. Metge, C. Fiorini-Debuisschert, F. Charra, M.-P. Teulade-Fichou, *J. Am. Chem. Soc.* **2008**, *130*, 16836–16837; e) C. Le Droumaguet, O. Mongin, M. H. V. Werts, M. Blanchard-Desce, *Chem. Commun.* **2005**, 2802–2804; f) Z. Fang, X. Zhang, Y. H. Laic, B. Liu, *Chem. Commun.* **2009**, 920–922; g) J. Wu, Y. Zhao, X. Li, M. Shi, F. Wu, X. Fang, *New J. Chem.* **2006**, *30*, 1098–1103; h) J. Shao, Z. Guan, Y. Yan, C. Jiao, Q.-H. Xu, C. Chi, *J. Org. Chem.* **2011**, *76*, 780–790; i) Y.-Z. Cui, Q. Fang, G. Xue, G.-B. Xu, L. Yin, W.-T. Yu, *Chem. Lett.* **2005**, *34*, 644–645; j) T.-C. Lin, Y.-J. Huang, Y.-F. Chen, C.-L. Hu, *Tetrahedron* **2010**, *66*, 1375–1382; k) Y. Jiang, Y. Wang, J. Hua, J. Tang, B. Li, S. Qian, H. Tian, *Chem. Commun.* **2010**, *46*, 4689–4691; l) O. Mongin, L. Porrès, T. Pons, C. Katan, J. Mertz, M. Blanchard-Desce, *Tetrahedron Lett.* **2003**, *44*, 8121–8125; m) L. Porrès, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2004**, *6*, 47–50; n) C. Katan, F. Terenziani, O. Mongin, M. H. V. Werts, L. Porrès, T. Pons, J. Mertz, S. Tretiak, M. Blanchard-Desce, *J. Phys. Chem. A* **2005**, *109*, 3024–3037; o) F. Terenziani, C. Le Droumaguet, C. Katan, O. Mongin, M. Blanchard-Desce, *ChemPhysChem* **2007**, *8*, 723–734.

[8] O. Mongin, R. K. Tathavarty, M. H. V. Werts, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Chem. Commun.* **2006**, 915–917.

[9] a) M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu, C. Xu, *Science* **1998**, *281*, 1653–1656; b) S.-J. Chung, M. Rumi, V. Alain, S. Barlow, J. W. Perry, S. R. Marder, *J. Am. Chem. Soc.* **2005**, *127*, 10844–10845; c) O. Mongin, L. Porrès, M. Charlot, C. Katan, M. Blanchard-Desce, *Chem. Eur. J.* **2007**, *13*, 1481–1498; d) S. Zheng, L. Beverina, S. Barlow, E. Zojer, J. Fu, L. A. Padilha, C. Fink, O. Kwon, Y. Yi, Z. Shuai, E. W. Van Stryland, D. J. Hagan, J.-L. Brédas, S. R. Marder, *Chem. Commun.* **2007**, 1372–1374; e) S. Zheng, A. Leclercq, J. Fu, L. Beverina, L. A. Padilha, E. Zojer, K. Schmidt, S. Barlow, J. Luo, S.-H. Jiang, A. K.-Y. Jen, Y. Yi, Z. Shuai, E. W. Van Stryland, D. J. Hagan, J.-L. Brédas, S. R. Marder, *Chem. Mater.* **2007**, *19*, 432–442; f) K. D. Belfield, M. V. Bondar, C. O. Yanez, F. E. Hernandez, O. V. Przhonska, *J. Mater. Chem.* **2009**, *19*, 7498–7502; g) L. Ventelon, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Chem. Commun.* **1999**, 2055–2056; h) O. Mongin, L. Porrès, L. Moreaux, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2002**, *4*, 719–722.

[10] a) B. R. Cho, K. H. Son, S. H. Lee, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J. H. Choi, H. Lee, M. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10039–10045; b) B. R. Cho, M. J. Piao, K. H. Son, H. L. Sang, J. Y. Soo, S.-J. Jeon, M. Cho, *Chem. Eur. J.* **2002**, *8*, 3907–3916.

[11] a) V. Z. Shirinian, A. A. Shimkin, *Top. Heterocycl. Chem.* **2008**, *14*, 75–105; b) A. V. Kulinich, A. A. Ishchenko, *Russ. Chem. Rev.* **2009**, *78*, 141–164.

[12] M. Barzoukas, M. Blanchard-Desce, *J. Chem. Phys.* **2000**, *113*, 3951–3959.

[13] V. A. Svetlichnyi, A. A. Ishchenko, E. A. Vaitulevich, N. A. Derevyanko, A. V. Kulinich, *Optics Commun.* **2008**, *281*, 6072–6079.

[14] a) A. O. Gerasov, M. P. Shandura, Y. P. Kovtun, *Dyes Pigments* **2008**, *77*, 598–607; b) L. A. Padilha, S. Webster, O. V. Przhonska, H. Hu, D. Peceli, J. L. Rosch, M. V. Bondar, A. O. Gerasov, Y. P. Kovtun, M. P. Shandura, A. D. Kachkovski, D. J. Hagan, E. W. Van Stryland, *J. Mater. Chem.* **2009**, *19*, 7503–7513.

[15] S. Webster, J. Fu, L. A. Padilha, O. V. Przhonska, D. J. Hagan, E. W. Van Stryland, M. V. Bondar, Y. L. Slominsky, A. D. Kachkovski, *Chem. Phys.* **2008**, *348*, 143–151.

[16] J. H. Chong, M. Sauer, B. O. Patrick, M. J. MacLachlan, *Org. Lett.* **2003**, *5*, 3823–3826.

[17] a) E. Fischer, Y. Hirshberg, *J. Chem. Soc.* **1952**, 4522–4524; b) G. Berkovic, V. Krongauz, V. Weiss, *Chem. Rev.* **2000**, *100*, 1741–1753; c) E. D. Bergmann, A. Wiezmann, E. Fischer, *J. Am. Chem. Soc.* **1950**, *72*, 5009–5012.

[18] W.-H. Lee, H. Lee, J. A. Kim, J.-H. Choi, M. Cho, S.-J. Jeon, B. R. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10658–10667.

[19] F. Terenziani, C. Sissa, A. Painelli, *J. Phys. Chem. B* **2008**, *112*, 5079–5087.

[20] a) L. Yu, A. Slominskii, I. D. Radchenko, *Chem. Het. Comp.* **1974**, *10*, 618–619; b) J. C. Mason, G. Patonay, L. Strekowski, *Heterocycl. Commun.* **1997**, *3*, 409–412; c) L. Strekowski, J. C. Mason, H. Lee, M. Sayand, G. Patonay, *J. Heterocycl. Chem.* **2004**, *41*, 227–232; d) G. Ponterinin, D. Vanossi, Z. A. Krasnaya, A. S. Tatokov, F. Momicchioli, *Phys. Chem. Chem. Phys.* **2011**, *13*, 9507–9517.

[21] a) H. Mustroph, K. Reiner, J. Mistol, S. Ernst, D. Keil, L. Hennig, *ChemPhysChem* **2009**, *10*, 835–840; b) H. Mustroph, J. Mistol, B. Senns, D. Keil, M. Findeisen, L. Hennig, *Angew. Chem.* **2009**, *121*, 8930–8933; *Angew. Chem. Int. Ed.* **2009**, *48*, 8773–8775.

[22] A. G. Anderson, P. J. Stang, *J. Org. Chem.* **1976**, *41*, 3034–3036.

[23] L. G. S. Brooker, F. L. White, *J. Am. Chem. Soc.* **1935**, *57*, 2480–2488.

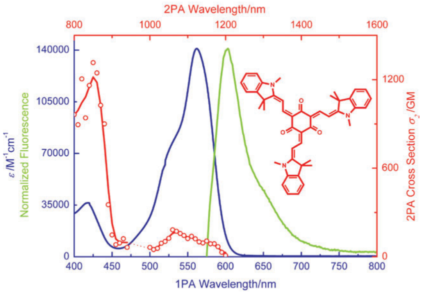
[24] M. Q. Doja, D. Prasad, *J. Indian Chem. Soc.* **1943**, *20*, 153.

Received: April 9, 2012

Dyes

Y. M. Poronik, V. Hugues, M. Blanchard-Desce, D. T. Gryko** .... ■■■■–■■■■

Octupolar Merocyanine Dyes: A New Class of Nonlinear Optical Chromophores



Octupolar merocyanine chromophores displayed very high molar absorption coefficients and high two-photon absorption cross-sections in the spectral range of interest for biological imaging. Changing the end heterocyclic moieties allowed the tuning of optical properties to approach the cyanine limit (i.e., polymethine state); this resulted in a red-shift of the linear absorption band, as well as in the rise of a two-photon band in the NIR region.