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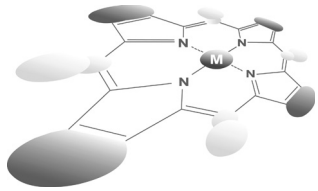

Corrole–imide dyads — Synthesis and optical properties

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Dedicated to Professor Shunichi Fukuzumi on the occasion of his retirement

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ABSTRACT: Two rarely seen building blocks have been incorporated into light absorbing arrays: corroles and 2,3-naphthalimides. General synthetic strategy consisting in direct condensation of formyl substituted aromatic imides with dipyrranes led to diverse range of *trans*-A_2B-corroles in acceptable yields. Spectroscopic properties of all five dyads studied suggest that regardless the imide's structure, components are weakly electronically coupled. Positioning 2,3-naphthaimide unit partially above the corrole core leads to slight alteration of their optical properties. Dyads bearing blue-absorbing imide components display different behavior depending on their structure. In corrole linked with naphthalenyl-naphthalene-1,8-carboximide a 100% effective energy transfer reaction from the imide component to the corrole component occurred. On the contrary, in small, strongly polarized amino-cyano-phthalimide neither efficient energy-nor electron-transfer could be detected and excitation leads to fluorescence from both components.

KEYWORDS: corroles, imide, synthesis, fluorescence, dipyrranes.

INTRODUCTION

The synthesis and photophysical characterization of multichromophoric arrays capable of energy and/or electron transfer have been one of the most exciting and fruitful areas of research in the last few decades [1]. The study of model systems mimicking the basic photochemical events in natural photosynthesis, often called "artificial photosynthesis," together with the crystallization of natural photosynthetic membrane complexes, considerably helped to establish the rules that govern the photoinduced processes observed in Nature [2]. Recently this basic subject has developed into a more advanced field which aims at light-driven water splitting and carbon-free fuel hydrogen production [3]. The interest in artificial photosynthesis is still growing, because an efficient conversion of sunlight into chemical energy or electricity might solve the rising environmental and energy supply problems. Furthermore, this research area is providing a deep insight into processes like photoinduced electronic energy transfer and electron transfer, which are of interest for a wide range of applications, from material chemistry to biology.

The majority of chromophores involved into natural photosynthesis belongs to the porphyrinoid class. Nature has chosen these tetrapyrrolic macrocycles to play such an important role because of their unique structure (aromatic 18 π-electron [18]-diazaannulene system), spectroscopic and redox properties, the ability of charge delocalization and formation of complexes with many metal cations. It is not surprising that the most frequently used building blocks for the construction of artificial multichromophoric arrays are *meso*- substituted porphyrins [4]. However, other porphyrinoids like chlorins [5], phthalocyanines [6] and subporphyrins [7] have been also used for this purpose. We recently incorporated another member of porphyrinoid family — corroles, into light harvesting

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arrays [8]. Corroles are one carbon short analogs of porphyrins with three *meso*-carbons between the four pyrrole rings. Because of structural similarity to corrin (macrocycle found in vitamin B_{12}) they attracted attention since early 60s of the last century [9], however, lack of efficient synthetic methodologies strongly hampered the progress in their chemistry. Nevertheless, recent discoveries in this area made them readily available [10], opening the door for various applications [11]. The analysis of spectroscopic, photophysical and electrochemical properties of *meso*-substituted corroles reveals that they exhibit more intense absorption of red light, larger Stokes shift, higher fluorescence quantum yields [12] and lower oxidation potentials [13], when compared to similarly substituted porphyrins. By taking advantage of these properties, we were able to achieve ultra-fast and efficient energy and electron transfer in corrole-fullerene [8f], corrole-aromatic imide [8b, 8i] and (aromatic) bisimide dyads and triads [8c, 8e, 8j, 8m]. Fullerenes and aromatic imides and bisimides are particularly convenient building blocks for multichromophoric arrays, because the former dye secures excellent charge separation lifetimes, whereas the latter is amenable for structural modifications, thus allowing an easy alteration of the properties of the resulting model systems. While working with the corrole-aromatic imide dyads and triads, we focused our attention on the very rare 2,3-naphthalimides. This type of chromophore, to the best of our knowledge, has never been used in the construction of light absorbing arrays, despite the structural similarity to broadly used 1,8-naphthalimides [8b, 14] and naphthalene-4,5:1,8-bis(dicarboximides) [15]. Attracted by the interesting photophysical properties of corrole-imide dyads, we set ourselves the difficult task of incorporation, for the first time, of 2,3-naphthalimides and few other less common aromatic imides into multichromophoric array. In spite of the development of new methodologies towards the synthesis of *meso*-substituted corroles, this could be a serious synthetic challenge, mostly due to solubility problems. In this paper we present the results of our synthetic efforts, the spectroscopic characterization of the prepared dyads and the basic photophysical properties.

RESULTS AND DISCUSSION

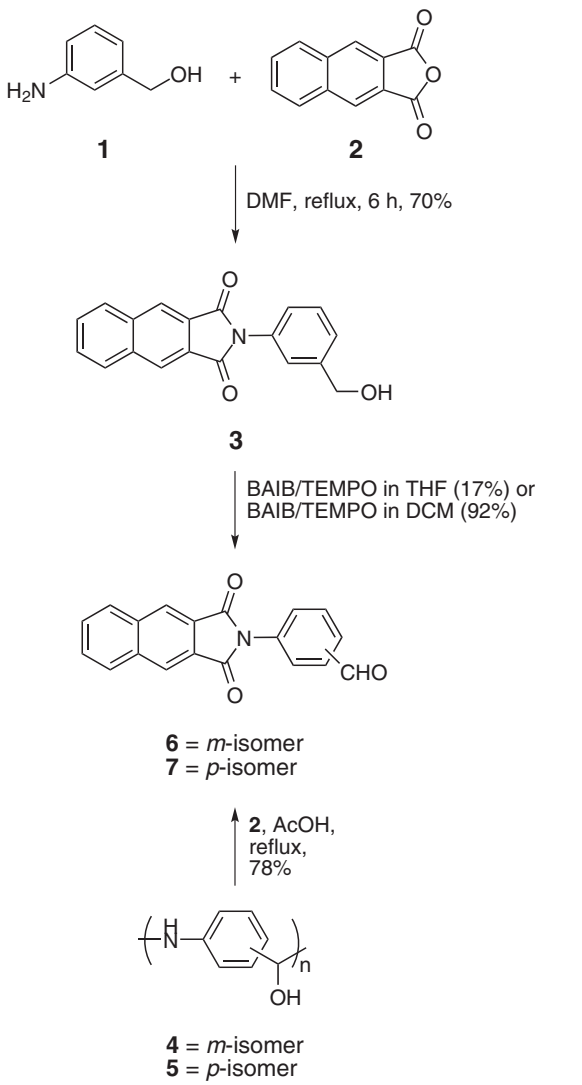
Design and synthesis

We were curious how spatial arrangement, especially strained face-to-face orientation of the dyad counterparts will influence its spectroscopic and photophysical properties. We required chromophore with elongated shape and absorption below 400 nm, so its absorption will not entirely overlap with Soret band of corroles. Consequently, we have chosen naphthalene-2,3-carboxyimide as a key structural element. In addition, we also designed to imides absorbing in violet-blue region. We would like one of them to possess large π-system without strong electron-withdrawing character and the second one very small but still possessing strong absorption between 400 and 450 nm. In order to synthesize *trans*-A_2B-corrole–imide dyads we decided to utilize the well-developed [2+1] condensation between dipyrranes and aldehydes. Given the moderate stability of corroles, we followed the general strategy starting from the preparation of an elaborated aldehyde which would then be used in the corrole forming reaction. Therefore our strategy was as follows: the synthesis of imide-derived aldehyde followed by final condensation with dipyrrane. In all cases 5-(pentafluorophenyl)dipyrrane was chosen, since previous studies showed that electron-withdrawing substituents are necessary to secure reasonable stability of final corrole [8b].

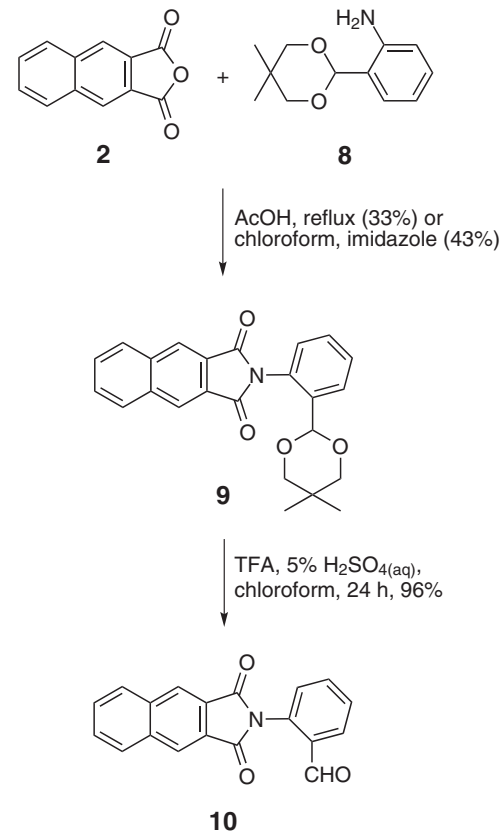
The shortest approach towards the necessary aldehydes would be to use aminobenzaldehydes and perform their direct condensation with the corresponding anhydrides. Such compounds, however, are generally unstable and even traces of acids initiate their polymerization. Therefore some kind of protection of an aldehyde functionality has to be used. We decided to investigate two approaches: protection of aldehyde in the form of acetal and the use of aminobenzyl alcohols as one oxidation level lower precursors for corresponding aldehydes. The latter option is justified by the fact that such alcohols are readily oxidized to corresponding aldehydes by a variety of methods. Thus, 2,3-naphthalenedicarboxylic acid anhydride (**2**) was reacted with 3-aminobenzyl alcohol in a boiling DMF and, after aqueous workup and flash chromatography purification, the desired alcohol **3** was obtained in 70% yield as a readily crystallizing solid. The solubility of the prepared alcohol in common organic solvents was rather low, presumably due to π-stacking and intermolecular hydrogen bond formation, and this fact complicated the search for appropriate conditions for oxidation reaction. The brief survey of oxidizing systems was made and in most cases either conversion was incomplete or complex mixtures arose. Surprisingly, oxidation of alcohol **3** with [bis(acetoxy)-iodo]benzene (BAIB)/TEMPO system [16] in dichloromethane gave target aldehyde **6** in a yield of 92%, though substrate was never dissolved and the reaction was performed in solid-to-solid regime, whereas better solubilizing solvent (THF) gave the expected product in much lower yield (17%) (Scheme 1).

Some time ago we found that 3-aminobenzaldehyde polymer reacts readily with 1,8-naphthalenedicarboxylic acid anhydride, forming the desired imidoaldehyde in one step [8b]. To our delight, anhydride of 2,3-naphthalenedicarboxylic acid exhibited similar reactivity against both 3-aminobenzaldehyde polymer (**4**) and 4-aminobenzaldehyde polymer (**5**), thus allowing straightforward, one step synthesis of aldehydes **6** and **7**.

According to our plan, *ortho*-substituted isomer of aldehydes **6** and **7** was one of the crucial substrates.



Scheme 1.



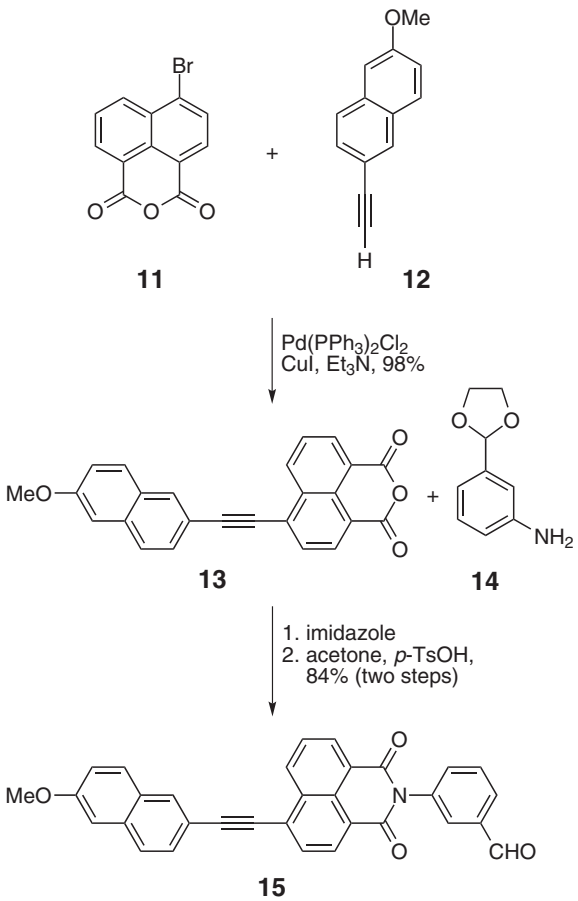
Scheme 2.

Therefore we synthesized acetal **9**, by the condensation of **8** with anhydride **2**. Among tested reaction conditions, boiling substrates in chloroform with an excess of imidazole gave the best results [17]. Subsequent deprotection of aldehyde function gave desired compound **10** (Scheme 2).

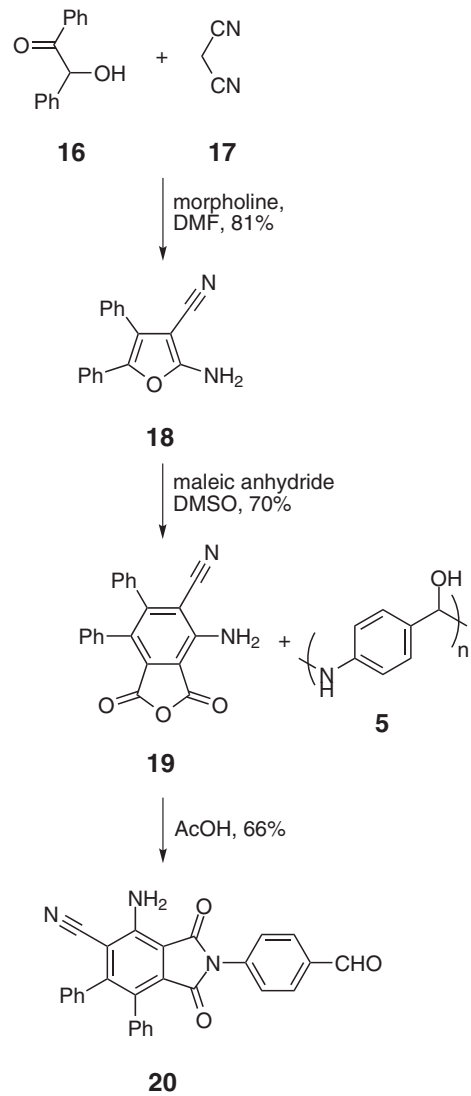
Aldehyde **15**, possessing skeleton unknown before, is particularly interesting, as its π-expanded structure can be characterized by strong donor–acceptor character, resulting in significant bathochromic shift of both absorption and emission maxima. Its synthesis was achieved in two steps starting from anhydride **11**. Sonogashira coupling with commercially available naphthalene-based arylacetylene **12**, followed by condensation of newly prepared anhydride **13** with 3-aminobenzaldehyde ethylene acetal (**14**) in imidazole/chloroform mixture, and deprotection step gave desired aldehyde **15** in excellent overall yield (Scheme 3).

Finally, continuing the search towards new small chromophores with interesting optical properties, derivatives of 3-amino-4-cyano-5,6-diphenylphthalimide were synthesized. Corresponding anhydride **19** was prepared according to published procedure [18]. Simple derivatives of this anhydride (phthaloyl hydrazide and *N*-hydroxy phthalimide) were described in the literature exclusively from the point of view of their biological activity (antitumor agents). Their spectroscopic properties were never studied and *N*-aryl-substituted imides of such type were unknown before our work. The combination of electron-withdrawing and electron-donating groups alters the electronic structure of organic chromophore decreasing the difference between HOMO and LUMO. As a result, anhydride **19** strongly absorbs violet-blue light. Assuming that free amino group will not cause complications during imide formation due to the combined effect of steric hindrance and its electron-poor character, anhydride **19** was used in further steps without modifications. In order to synthesize the necessary aldehyde, the mixture of anhydride **19** and *p*-aminobenzaldehyde polymer (**5**) was refluxed in acetic acid. Aldehyde **20** was obtained with good yield and acceptable purity without chromatographic purification (Scheme 4).

With a small library of aromatic aldehydes, precursors for corrole synthesis, we began a dyads' synthesis. We have chosen the reaction conditions optimized for corroles



Scheme 3.



Scheme 4.

bearing electron-withdrawing substituents, which were elaborated in our group [10j]. The reactions were performed in dichloromethane as a solvent with TFA concentration of *ca*. 13 mM. After bilane (the linear tetrapyrrolic corrole precursor) formation, the oxidation step was performed with DDQ. Under these conditions we were able to obtain five corrole-aromatic imide dyads, usually in moderate yield (14–18%). Only corrole **26** was formed in lower yield (6%, Table 1). Among possible unfavorable factors, free amino group of aldehyde was considered to be a site which is capable to bind acidic catalyst and hence reduce its active concentration in the reaction mixture. Having this in mind, reaction was repeated with doubled concentration of TFA (*ca*. 27 mM) but, unfortunately, it did not improve outcome of the experiment.

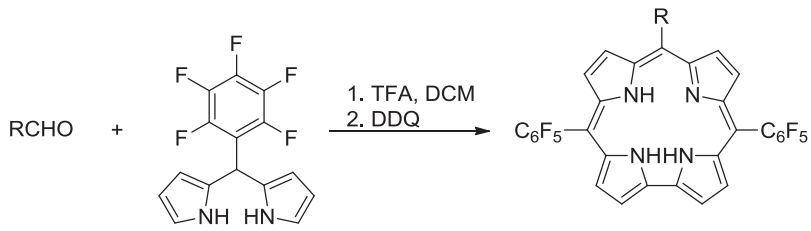
Finally, imides **28** and **29** and corrole **30** were prepared and used for photophysical studies as model compounds lacking additional chromophore (Scheme 5). All prepared corroles were sufficiently stable both in solid state and in solution, thus allowing their spectroscopic characterization.

Spectroscopic characterization of prepared dyads

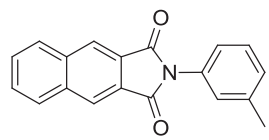
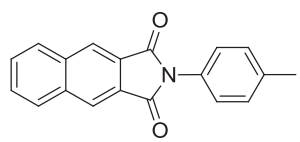
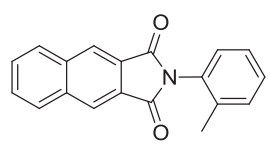
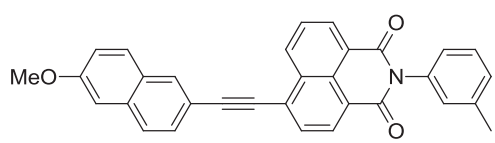
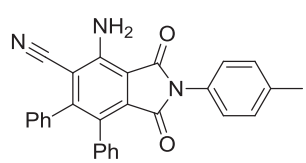
The five corrole-based dyads have been studied in toluene (TOL) solutions at room temperature along with their imides and corrole models, **28**, **29**, **13** and **30** respectively. Corrole **30** has been previously extensively investigated by our groups [12a] and often used as model for corrole containing multi-component systems [8a, 8c, 8e].

Dyads 22, 23, 24. The absorption spectra of dyads **22**–**24** are reported in Fig. 1 overlaid to those of the corresponding models. These dyads differ for the linking position (*ortho*, *meta*, *para*) of the imide to the corrole and one of the aims of our study was to detect differences in their spectroscopic and photophysical properties. Naphthalene-imide **28** displays a structured absorption band with maxima at 358 and 341 nm with a molar absorption coefficient <3,000 $M^{-1}.cm^{-1}$, whereas corrole **30** has an intense Soret band at 419 nm (ε = 120,000 $M^{-1}.cm^{-1}$) and weaker Q-bands at 523, 562, 617 and 640 nm (ε < 20,000 $M^{-1}.cm^{-1}$). As can be seen from Fig. 1, the spectra of the *meta* and *para* dyads **22** and **23** are

Table 1. Synthesis of corrole–aromatic imide dyads



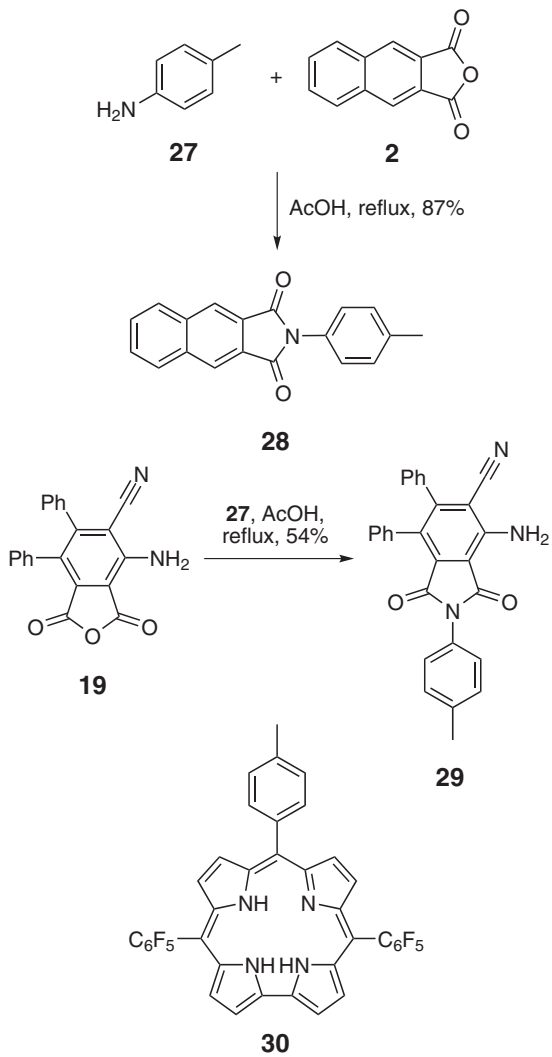
21 **22-26**

Aldehyde	Corrole	R	Yield, %
6	**22**		16
7	**23**		14
10	**24**		17
15	**25**		18
20	**26**		6

perfectly superimposable to the plain superposition of the component models **28** and **30** (Figs 1a and 1b). They in fact display additivity both in the UV, where the imide **28** bands position and intensity are well-reproduced and at lower energies, where the Soret and Q-bands of corrole **30** are perfectly overlapped. This is an indication of a poor electronic coupling of the component units in the dyads. On the contrary the *ortho* isomer **24** displays poor additivity (Fig. 1c) which can be noticed predominantly in the region of corrole absorbance, in the intensity of the 419 nm Soret band and in the lowest energy Q-band at 640 nm, which is missing in the dyad. However, also in the UV region where the imide bands are discernible, the total absorbance is lower than expected on the basis of a plain additivity. The behavior of the *ortho* dyad **24** is ascribed to a perturbation induced by the positioning of aromatic system over the corrole ring.

The luminescence properties of dyads **22**–**24** were examined in detail in order to ascertain whether the photoinduced processes were affected by the substitution type. The imide model **28** displays a broad emission spectrum with maximum at 501 nm and a weak luminescence yield with Φ_{fl} = 0.011 and corrole **30** shows a more intense luminescence with Φ_{fl} = 0.14 after excitation on the respective bands (Table 2).

The dyads, after excitation in the imide band at 358 nm displayed a luminescence which was essentially that of corrole (Fig. 2). The luminescence of the imide moiety is almost completely quenched (<97%) whereas the corrole band appears sensitized by a value of *ca*. 20% in the isomers **22** and **23**. On the contrary, the emission of the corrole unit in the *ortho* isomer **24** has an intensity identical to that of corrole. This indicates that in the decoupled dyads **22** and **23** a complete energy transfer from the imide moiety to the corrole occurs, in fact 20% is also the amount of photons absorbed by the donor imide at the excitation wavelength, see absorption spectra. For dyad **24**, characterized as discussed above



Scheme 5.

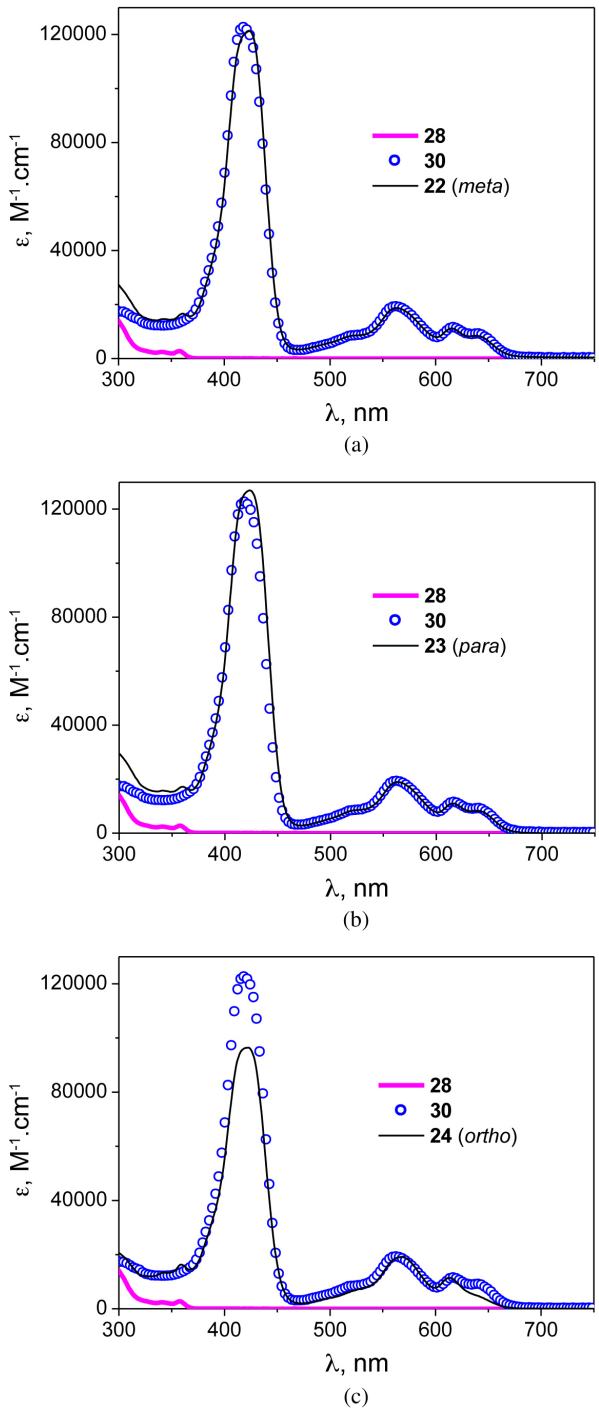


Fig. 1. Absorption spectra of dyads **22**, **23** and **24** in TOL overlaid with those of the models **28** and **30**

by some electronic interaction because of the geometric arrangement, the sensitization is not clearly detected. However, an excitation spectrum registered at 660 nm, where only corrole moiety emits, indicate the presence of the bands of the imide (Fig. 3), showing that also in this case energy transfer occurs.

Excitation of the corrole unit in the dyads leads to an emission identical to that of the model in dyads **22** and **23**, whereas in the *ortho* derivative **24** there is a quenching of the order of 20% (data not shown). Time resolved experiments after 355 nm excitation shows that in all dyads the lifetime of the model imide measured at 500 nm, 1.6 ns in the model, is reduced to 55 ± 5 ps, identical within experimental uncertainty, whereas the lifetime of corrole moiety measured at 660 nm is identical to that of the models for all dyads, 3.85 ± 0.5 ns. These data allow to calculate a rate of energy transfer from the imide to the corrole moiety of the order of 1.8×10^{10} s^{-1} for all dyads. Such a high rate is not surprising given the strong overlap between the emission of donor **28** and the absorption of acceptor **30**, a critical parameter for the occurrence of energy transfer. The "strange" behavior of the *ortho* dyad **24**, which appears to have a lower emission yield from the corrole unit than the model and the other dyads might be ascribable to the electronic perturbation brought about by the close packing of the two chromophores which are expected to alter the radiative parameters. However we cannot completely exclude the hypothesis that a through

Table 2. Luminescence parameters of dyads **22–24** and pertinent models in TOL at room temperature

	λ^{em}_{max}, nm[a]	Φ^{b}_{fl}	Φ^{c}_{fl}	τ, ns
28	501	0.011		1.6
30	656, 716		0.14[d]	3.8[d]
22	660, 716	<0.0001, 0.16	0.14	0.054; 3.8
23	661, 717	<0.0001, 0.17	0.14	0.060; 3.9
24	661, 715	0.0003, 0.14	0.11	0.050; 3.9

[a]Data from corrected spectra. [b]Luminescence quantum yield, excitation in the imide band (350 nm). [c]Luminescence quantum yield, excitation in the corrole band (560 nm). [d]Data from Ref. 12a.

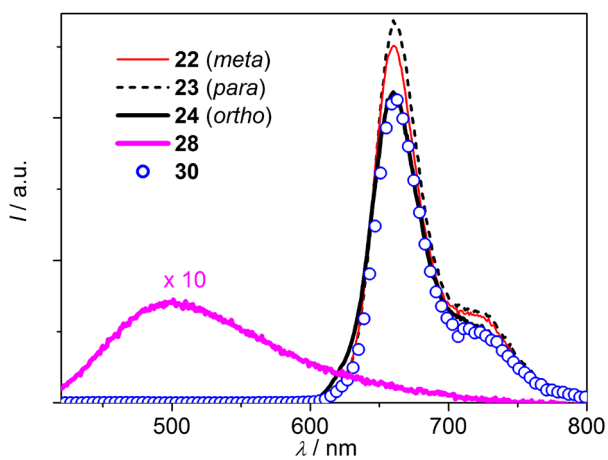


Fig. 2. Fluorescence spectra in TOL of dyads **22**, **23** and **24** and models after excitation at 358 nm (optically matched solutions with $A = 0.09$)

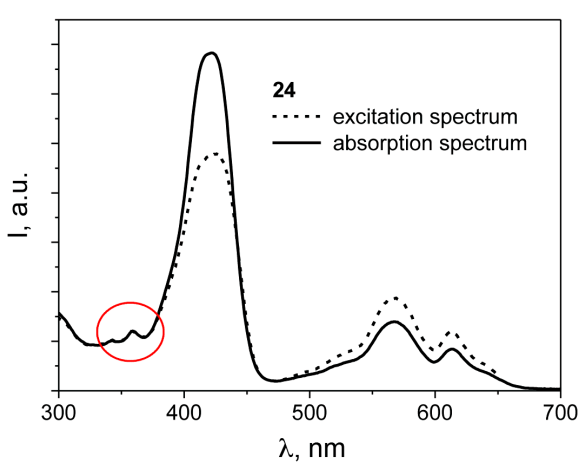


Fig. 3. Arbitrarily scaled absorption and excitation spectra of **24** in TOL. The excitation spectrum has been recorded at 660 nm

space electron transfer can occur with low efficiency in such a close packing of donor (**30**) and acceptor (**28**) both *via* LUMO–LUMO (when corrole is excited) than *via* HOMO–HOMO (when the imide is excited) mechanisms.

Therefore, from the present data there is no clear evidence that the different types of substitution either *ortho*, *meta* or *para*, affect the nature or the rate of the photoinduced processes. It can however be noticed that in the *ortho* isomer **24** the proximity of the electronic clouds of the two moieties due to the positioning of the imide over the tetrapyrrolic ring, induces an electronic interaction leading to a variation in spectroscopic parameters.

Dyads 25 and 26. The absorption spectra of the dyads and the related models **13**, **29** and **30** are reported in Fig. 4. Due to the low amount of compound available, the molar absorption coefficients might be affected by some uncertainty. Imide **13** displays a structured band with maxima at 403 and 417 nm (ε *ca.* 27,000 $M^{-1}.cm^{-1}$) and **29** displays a broad absorption band around 415 nm, with an ε = 10,000 $M^{-1}.cm^{-1}$, in agreement with similar compounds [19]. The dyad spectra appear to be the simple superposition of the component units within experimental errors, indicating that the level of electronic interaction between the components is weak.

The photophysics of these dyads was examined with a lower detail in comparison to the former ones. The

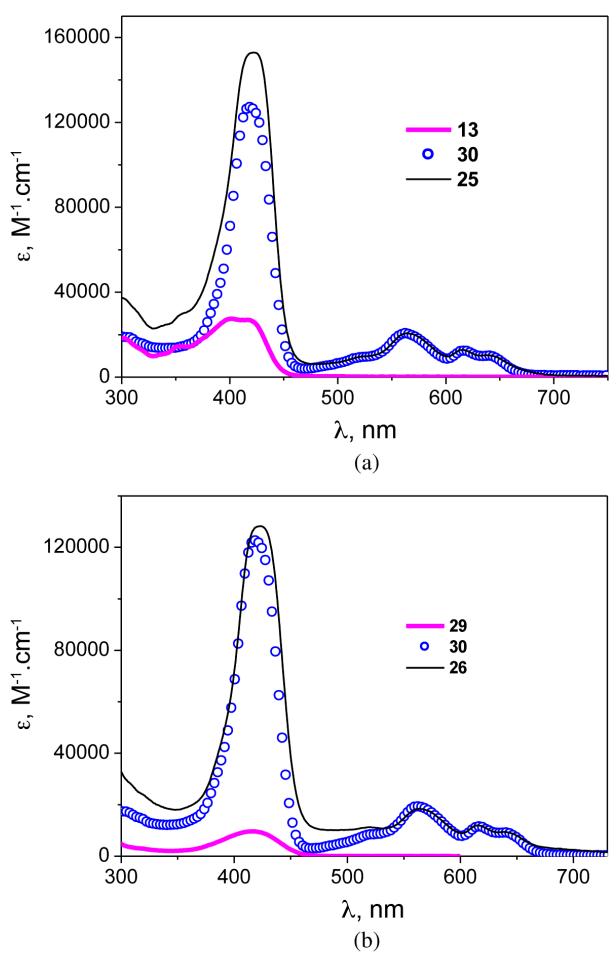


Fig. 4. Absorption spectra of dyads **25** and **26** in TOL overlaid with those of the models **13, 29** and **30**

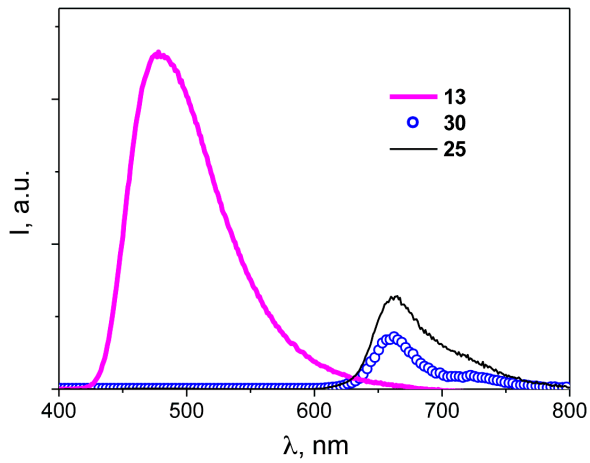


Fig. 5. Fluorescence spectra in TOL of dyad **25** and models after excitation at 350 nm (optically matched solutions with $A = 0.07$)

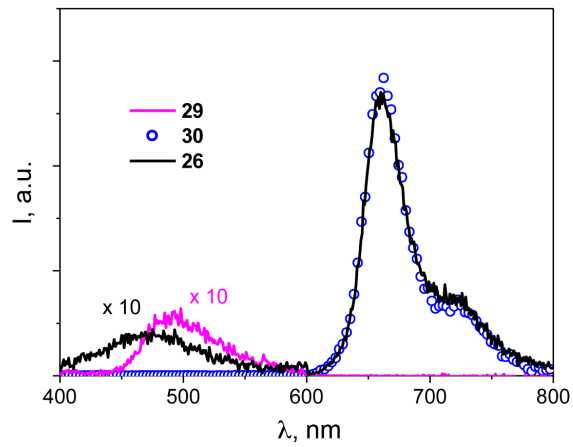


Fig. 6. Fluorescence spectra in TOL of dyad **26** and models after excitation at 350 nm (optically matched solutions with $A = 0.07$). The luminescence intensity of **26** is multiplied by 10 only in the 400–600 nm range

emission spectra of dyad **25** and of optically matched models **13** and **30** after excitation at 350 nm are reported in Fig. 5. The fluorescence of reference **13** maximizes at 478 nm and is quite high compared to the other imide components (luminescence quantum yield close to 1), but not unusual for this type of structures [19]. The luminescence of the imide is totally quenched in the dyad whereas the luminescence of the corrole unit is sensitized by a factor of 2. By taking into account that at 350 nm the imide component absorbs *ca*. 50% of the incident photons (see Fig. 4a), the observed phenomena can be interpreted by a 100% effective energy transfer reaction from the imide component to the corrole component. Selective excitation of the dyad on the corrole band at 560 nm leads to a luminescence identical to that of the model corrole (data not shown).

Figure 6 illustrates the luminescence spectra of **26** and model components. The imide **29** displays a very weak luminescence, with λ_{max} at 495 nm, similar to the one of the previously seen model **28**. Excitation of **26** at 350 nm leads to a luminescence from the imide units reduced to about 80% of that of the model **29**, accompanied by a 20 nm hypsochromic shift. No sensitization or quenching was noticed in the luminescence of the corrole moiety with respect to **30** upon excitation at the same wavelength. A selective excitation at 560 nm where only the corrole absorbs, led to a luminescence decrease of this unit in the dyad to *ca*. 80% compared to the model (data not shown). The results are not so clear-cut as the former one. The photoinduced processes, which might be a combination of energy and electron transfer are however rather inefficient, leaving the luminescence of both components almost unaffected. A more detailed examination involving time resolved absorption techniques would be necessary in order to elucidate the detailed mechanism.

EXPERIMENTAL

General

All commercially available compounds were used without additional purification, unless otherwise noted. Organic solvents were purified according to generally accepted literature methods [20]. Reactions involving air and/or moisture sensitive reagents were performed under inert atmosphere (argon). Reactions progress was controlled by thin layer chromatography (TLC), performed on commercially available aluminum plates covered with silica gel or neutral aluminum oxide (60 F254, Merck). All R_f values are referred to SiO_2. For the purification by the means of column chromatography silica gel 60 (Merck) was used. Dry column vacuum chromatography was performed on MN-Silica gel P/UV254 for preparative chromatography. Size exclusion column (SEC) was filled with BioRad Bio-Beads SX-1 and eluted with either THF or toluene. Melting points were measured on Automatic Melting Point Apparatus (EZ-Melt, Stanford Research Systems) and are presented without correction. Structure and purity of synthesized compounds was confirmed using ^{1}H, ^{13}C NMR, MS and elemental analysis (all values are given as percentages). NMR spectra were obtained on Varian Mercury 400 MHz, Bruker DRX500 MHz, Varian VNMRS 500 MHz or 600 MHz. Reported chemical shifts (δ, ppm) were determined relative to TMS as the internal reference. Mass spectra were obtained on AMD-604 (AMD Intectra GmbH), Mariner (Perseptive Biosystems, Inc.), 4000 Q-TRAP (Applied Biosystems) or GCT Premier (Waters). Some compounds were synthesized following literature procedures: **8** [21], **14** [22], **19** [18], **30** [10j]. Compounds **1**, **2**, **4**, **5**, **11**, **12**, **16**, **17**, **27** were commercially available and used without further purification.

Synthesis

Preparation of 2-(3-(hydroxymethyl)phenyl)-benzo-[f]isoindole-1,3-dione (3). The solution of 2,3-naphthalenedicarboxylic acid anhydride (**2**, 1.98 g, 10 mmol) and 3-aminobenzyl alcohol (**1**, 1.23 g, 10 mmol) in DMF (50 mL) was heated under reflux for 6 h. After cooling the reaction mixture to ambient temperature water (50 mL) was added. The precipitate was filtered off, washed with small amount of EtOH and chromatographed (SiO_2, CH_2Cl_2 + 2%MeOH) affording **3** (2.11 g, 70%) as colorless crystals. mp 214–215 °C. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ, ppm 4.59 (2H, d, J = 5.8 Hz, CH_2), 5.35 (1H, t, J = 5.8 Hz, OH), 7.36 (1H, d, J = 8.0 Hz, C_6H_4), 7.42 (1H, d, J = 8.0 Hz, C_6H_4), 7.45 (1H, s, C_6H_4), 7.51 (1H, t, J = 8.0 Hz, C_6H_4), 7.81 (2H, m, naphth), 8.30 (2H, m, naphth), 8.60 (2H, s, naphth). ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ, ppm 62.9, 125.2, 125.7, 126.1, 126.6, 127.8, 129.0, 129.8, 130.7, 132.4, 135.6, 144.0, 167.2. Anal. calcd. for $C_{19}H_{13}NO_3$: C, 75.24; H, 4.32; N, 4.62; found C, 75.23; H, 4.45; N, 4.54. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{19}H_{13}NO_3$, 303.0895; found 303.0900.

Preparation of 3-(1,3-dioxo-1,3-dihydrobenzo[f] isoindol-2-yl)benzaldehyde (6). ***Method A.*** Alcohol **3** (660 mg, 2.18 mmol) was suspended in the solution of TEMPO (34 mg, 10% mol) in DCM (5 mL). Subsequently, BAIB (772 mg, 2.4 mmol) was added and the reaction mixture was stirred until the alcohol was fully consumed (nearly 3 h). The reaction mixture was diluted with DCM to dissolve solid product, washed with saturated $Na_2S_2O_3$ aq and extracted with DCM (3 × 10 mL). The combined organic extracts were washed with $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography (silica, DCM/hexanes 4:1) afforded title compound as a colorless crystalline solid (610 mg, 92%). ***Method B.*** 2,3-naphthalenedicarboxylic acid anhydride (**2**, 991 mg, 5 mmol) and 3-aminobenzaldehyde polymer (**4**, 605 mg, 5 mmol) were suspended in acetic acid (12 mL) and stirred at reflux overnight. The precipitate, formed after cooling to rt, was filtered off, washed with AcOH and dried under vacuum (1.18 g, 78%). R_f 0.4 (DCM). mp 281°C (decomposed). ^{1}H NMR (600 MHz, DMSO-d_6, TMS): δ, ppm 7.78–7.85 (3H, m, C_6H_4 + naphth), 7.87 (1H, m, C_6H_4), 8.02 (1H, m, C_6H_4), 8.07 (1H, m, C_6H_4), 8.33 (2H, m, naphth), 8.67 (2H, s, naphth), 10.10 (1H, s, CHO). ^{13}C NMR (150 MHz, DMSO-d_6, TMS): δ, ppm 124.9, 127.3, 127.3, 129.3, 129.7, 130.2, 132.9, 133.0, 135.1, 136.7, 166.4, 192.5. Anal. calcd. for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65; found C, 75.63; H, 3.71; N, 4.58. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{19}H_{11}NO_3$, 301.0739; found 301.0724.

Preparation of 4-(1,3-dioxo-1,3-dihydrobenzo[f]-isoindol-2-yl)benzaldehyde (7). 2,3-Naphthalenedicarboxylic acid anhydride (**2**, 1.98 g, 10 mmol) and 4-aminobenzaldehyde polymer (**5**, 1.21 g, 10 mmol) were suspended in acetic acid (25 mL) and stirred at reflux overnight. Orange color disappeared (reaction mixture becomes yellow). The precipitate, formed after cooling to rt, was filtered off, washed with AcOH and dried under vacuum (2.38 g, 79%). R_f 0.3 (DCM). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ, ppm 7.79 (2H, d, J = 8.4 Hz, C_6H_4), 7.82 (2H, m, naphth.), 8.10 (2H, d, J = 8.4 Hz, C_6H_4), 8.33 (2H, m, naphth.), 8.67 (2H, s, naphth.), 10.09 (1H, s, CHO). ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ, ppm 125.5, 127.7, 128.0, 130.0, 130.4, 130.8, 135.6, 135.7, 137.8, 166.7, 192.9. Anal. calcd. for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65; found C, 75.68; H, 3.68; N, 4.63. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{19}H_{11}NO_3$, 301.0739; found 301.0729.

Preparation of 2-[2-(5,5-dimethyl-[1,3]dioxan-2-yl)-phenyl]benzo[f]isoindole-1,3-dione (9). ***Method A.*** The mixture of 2,3-naphthalenedicarboxylic anhydride (**2**, 420 mg, 2.12 mmol) and 2-aminobenzaldehyde acetal **8** (482 mg, 2.33 mmol) in AcOH (5 mL) was stirred at 110 °C overnight. After cooling to rt and solvent evaporation, the residue was dissolved in DCM, washed with $NaHCO_3$ aq, dried over Na_2SO_4 and chromatographed (AcOEt/hexanes 1:3) giving 273 mg (33%) of acetal **9**. ***Method B.*** 2,3-naphthalenedicarboxylic anhydride (**2**, 990 mg, 5 mmol), acetal **8** (1.55 g, 7.5 mmol) and imidazole (6.8 g, 0.1 mol) were loaded into 100 mL round-bottom flask and chloroform (40 mL) was added. The mixture was stirred at gentle reflux for 2 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 15 min and then filtered. Filter cake was washed with cold ethanol and air-dried. Column chromatography (DCM/hexanes 3:1) afforded 838 mg (43%) of **9** as a colorless solid. R_f 0.5 (DCM/hexanes 3:1). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ, ppm 0.61 (3H, s, CH_3), 1.10 (3H, s, CH_3), 3.39 (2H, d, J = 10.9 Hz, CH_2), 3.55 (2H, d, J = 11.1 Hz, CH_2), 5.42 (1H, s, CH), 7.29 (1H, m, C_6H_4), 7.51 (2H, m, C_6H_4), 7.74 (2H, m, naphth.), 7.85 (1H, m, C_6H_4), 8.11 (2H, m, naphth.), 8.47 (2H, s, naphth.). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ, ppm 21.7, 23.0, 30.1, 77.6, 99.0, 125.2, 127.7, 127.9, 129.3, 129.4, 129.5, 129.6, 129.7, 130.3, 135.6, 136.2, 167.2. Anal. calcd. for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62; found C, 74.13; H, 5.36; N, 3.58. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{24}H_{21}NO_4$, 387.1471; found 387.1478.

Preparation of 2-(1,3-dioxo-1,3-dihydro-benzo[f] isoindol-2-yl)-benzaldehyde (10). TFA (8 mL) and 5% H_2SO_4 were added to acetal **9** (1 mmol) dissolved in 20 mL of chloroform and the reaction mixture was stirred for 24 h at rt. The reaction mixture was diluted with water (50 mL) and allowed to stir for the next 30 min. The mixture was extracted with chloroform (3 × 10 mL), washed with 2 M $NaHCO_3$, dried over $MgSO_4$ and concentrated. Residue was recrystallized from chloroform to give crystalline product (96%). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ, ppm 7.67 (1H, d, J = 7.8 Hz, C_6H_4), 7.76 (1H, t, J = 7.5 Hz, C_6H_4), 7.83 (2H, m, naphth.), 7.89 (1H, m, C_6H_4), 8.08 (1H, m, C_6H_4), 8.33

(2H, m, naphth.), 8.67 (2H, s, naphth.), 10.04 (1H, s, CHO). ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ, ppm 125.6, 128.0, 130.0, 130.1, 130.7, 130.8, 131.5, 132.5, 132.7, 135.2, 135.7, 167.4, 191.7. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{19}H_{11}NO_3$, 301.0739; found 301.0743.

Preparation of 4-(6-methoxynaphthalen-2-ylethynyl)-1,8-naphthalenedicarboxylic anhydride (13). A 100 mL round-bottom flask containing a magnetic stirbar was charged with 4-bromo-1,8-naphthalic anhydride (**11**, 830 mg, 3 mmol), triphenylphosphine (16 mg, 0.06 mmol), copper(I) iodide (5.7 mg, 0.03 mmol), bis(triphenylphosphine)palladium dichloride (2.1 mg, 3 μmol), and 15 mL of triethylamine. 2-Ethynyl-6-methoxynaphthalene (**12**, 656 mg, 3.6 mmol) was added to the flask with 30 mL of toluene. A condenser containing a nitrogen inlet was placed attached, and the reaction mixture was heated to reflux for 14 h. The reaction mixture was cooled and filtered. The filtercake was washed with toluene and dried at 80 °C under vacuum. At this point the yield of a crude product, yellow amorphous solid contaminated with small amount of starting anhydride, was 1.11 g (98%) and it was used in the next step without any further purification. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{25}H_{14}O_4$, 378.0892; found 378.0900.

Preparation of aldehyde 15. The mixture anhydride **13** (756 mg, 2 mmol), 3-aminobenzaldehyde ethylene acetal (**14**, 396 mg, 2.4 mmol) and imidazole (6.8 g, 0.1 mol) in chloroform (40 mL) was stirred at gentle reflux for 12 h and then cooled to rt. The solvent was removed on rotary evaporator and the residue was taken up in small amount of absolute ethanol. The resulting suspension was sonicated for 10 min, filtered, washed with cold ethanol and dried under vacuum. NMR analysis revealed the mixture of aldehyde and acetal and the sample was fully deprotected by stirring it with excess of acetone in the presence of *p*-TsOH (35 mmol/L). The product was purified by gravity column chromatography (DCM/acetone 98:2), furnishing aldehyde **15** as a bright yellow solid (811 mg, 84%). mp 222–3 °C. Anal. calcd. for $C_{34}H_{23}NO_5$: C, 77.70; H, 4.41; N, 2.68; found C, 77.85; H, 4.34; N, 2.66. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{34}H_{23}NO_5$, 525.1576; found 525.1564.

Preparation of 4-amino-1,3-dioxo-6,7-diphenyl-2-p-formylphenyl-2,3-dihydro-1H-isoindole-5-carbonitrile (20). Anhydride **19** (1.8 g, 5.3 mmol) and p-aminobenzaldehyde polymer (**5**, 770 mg 6.36 mmol) were suspended in AcOH (14 mL) and the reaction mixture was stirred at reflux overnight. Orange color of aminobenzaldehyde disappeared and reaction was cooled to rt. Yellow solid was filtered off, washed with small amount of AcOH and dried under vacuum, giving 1.54 g (66%) of aldehyde **20**. R_f 0.4 (DCM). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ, ppm 6.20 (2H, br s, NH_2), 7.00–7.05 (2H, m, Ph), 7.09–7.14 (2H, m, Ph), 7.17–7.24 (3H, m, Ph), 7.24–7.31 (3H, m, Ph), 7.65 (2H, m, C_6H_4), 7.97 (2H, m, C_6H_4), 10.03 (1H, s, CHO). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ, ppm 104.0, 110.4, 114.9, 126.3, 127.7, 128.2, 128.9, 129.1, 129.4, 129.7, 130.2, 130.3, 131.6, 133.4, 135.1, 135.8, 136.6, 146.6, 154.4, 165.0, 167.1, 191.1. Anal. calcd. for $C_{28}H_{17}N_3O_3$: C, 75.84; H, 3.86; N, 9.48; found C, 75.94; H, 3.88; N, 9.44. HRMS-EI: *m/z* $[M]^{\bullet+}$ calcd. for $C_{28}H_{17}N_3O_3$, 443.1270; found 443.1257.

Preparation of corrole dyad 22. Aldehyde **6** (0.6 g, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (**21**, 1.25 g, 4 mmol) were suspended in 30 mL of DCM and 330 μL of preprepared TFA solution (from now on this solution will be referred as "TFA stock solution," 10 mL of TFA in 100 mL of DCM) was added. The reaction course was controlled by TLC and after 30 min, the reaction was quenched by triethylamine addition (60 μL). The reaction mixture was diluted to 200 mL with DCM and poured into solution of DDQ (1.18 g, 5.2 mmol) in 300 mL of DCM stirred vigorously. After 2 h, the reaction mixture was slightly concentrated and passed through 2 cm silica pad. Product-containing fractions (contaminated by dipyrrin) were combined and solvent was removed under reduced pressure. Residue was washed with small amount of methanol, suspended in boiling cyclohexane and after cooling, crystals were filtered off and dried under vacuum giving 288 mg of corrole **22** (16%). R_f 0.4 (DCM/hexanes 3:2). UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 613 (13.5), 563 (13.5), 422 (127.7). ^{1}H NMR (500 MHz, THF-d_8, TMS): δ, ppm (-4)–(-1.5) (3H, br s, NH), 7.72 (2H, m, naphth.), 7.90–7.97 (2H, m, C_6H_4), 8.19 (2H, m, naphth.), 8.25 (1H, m, C_6H_4), 8.47 (1H, m, C_6H_4), 8.55 (2H, s, naphth.), 8.59 (2H, br s, β-H), 8.84 (2H, br s, β-H), 8.87 (2H, d, J = 4.5 Hz, β-H), 9.09 (2H, d, J = 3.7 Hz, β-H). HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found 902.1646.

Preparation of corrole dyad 23. Aldehyde **7** (0.6 g, 2 mmol) and 5-(pentafluorophenyl)dipyrrane (**21**, 1.25 g, 4 mmol) were suspended in 30 mL of DCM and 330 μL of TFA stock solution (see above) was added. The reaction course was controlled by TLC and after 30 min, the reaction was quenched by triethylamine addition (60 μL). The reaction mixture was diluted to 200 mL and poured into solution of DDQ (1.18 g, 5.2 mmol) in 300 mL DCM stirred vigorously. After 2 h, the reaction mixture was slightly concentrated and passed through 2 cm silica pad. Product-containing fractions were combined and solvent was removed under reduced pressure. Residue was washed with small amount of methanol, suspended in boiling cyclohexane and after cooling, crystals were filtered off and dried under vacuum giving 244 mg of corrole **23** (14%). R_f 0.33 (DCM/hexanes 2:1). UV-vis (DCM): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 615 (12.4), 564 (11.3), 419 (118.3). ^{1}H NMR (500 MHz, THF-d_8, TMS): δ, ppm (-4)–(-1.5) (3H, br s, NH), 7.78 (2H, m, naphth.), 8.02 (2H, m, C_6H_4), 8.25 (2H, m, naphth.), 8.35 (2H, m, C_6H_4), 8.63 (4H, m, naphth.+β-H), 8.74 (2H, br s, β-H), 8.82 (2H, br s, β-H), 9.10 (2H, br s, β-H). HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found 902.1618.

Preparation of corrole dyad 24. The mixture of aldehyde **10** (311 mg, 1.03 mmol) and

5-(pentafluorophenyl)dipyrrane (**21**, 645 mg, 2.06 mmol) in 15 mL of DCM was treated with 170 μL of TFA stock solution (see above). After 20 min, the reaction was quenched with 30 μL of triethylamine, diluted with DCM to 130 mL and DDQ (608 mg, 2.68 mmol) dissolved in a minimal amount of toluene was added. After 2 h of stirring, the reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (DCM/hexanes 1:4 → 1:1). Product-containing fractions were collected and evaporated. Crystallization from DCM afforded 157 mg (17%) of corrole **24** as a crystalline solid. R_f 0.4 (DCM/hexanes 3:2). UV-vis (THF): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 296 (22.9), 419 (11.7), 561 (19.4), 611 (11.0). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ, ppm 7.27 (m, naphth.), 7.48 (2H, m, naphth.), 7.61 (2H, s, naphth.), 7.82 (1H, m, C_6H_4), 7.89 (1H, m, C_6H_4), 7.97 (1H, m, C_6H_4), 8.25 (1H, m, C_6H_4), 8.42 (2H, br s, β-H), 8.66 (2H, d, J = 5.9 Hz, β-H), 8.81 (2H, d, J = 6.0 Hz, β-H), 8.91 (2H, br s, β-H). HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{49}H_{22}N_5O_2F_{10}$, 902.1608; found 902.1579.

Preparation of corrole dyad 25. To the mixture of aldehyde **15** (770 mg, 1.6 mmol) and 5-(pentafluorophenyl)dipyrrane (**21**, 1 g, 3.2 mmol) in 24 mL of DCM, 260 μL of TFA stock solution (see above) was added while stirring. The reaction was very slow and it was left to stirr overnight, then quenched with 45 μL of triethylamine. After dilution with DCM to 300 mL, DDQ (944 mg, 4.16 mmol), dissolved in a minimal amount of toluene, was added and the reaction mixture was stirred for 2 h. Subsequently, the reaction mixture was passed through silica pad, evaporated with Celite and chromatographed (DCM/hexanes 3:1). There were additional spots with similar polarity and the sample was submitted to SEC purification (eluted with THF). Product-containing fractions were collected and evaporated. Crystallization from DCM afforded 320 mg (18%) of corrole **25** as a crystalline solid. R_f 0.4 (DCM/hexanes 3:1). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 431 (157), 561 (17.1), 614 (12.2), 647 (7.9). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ, ppm (-4)–(-1.5) (3H, br s, NH), 3.95 (3H, s, OCH_3), 7.15 (1H, m, $C_{10}H_6$), 7.20 (1H, m, $C_{10}H_6$), 7.67 (1H, m, $C_{10}H_6$), 7.76 (3H, m, C_6H_4+$C_{10}H_6$), 7.89–8.00 (2H, m, C_6H_4+naphth.), 8.04 (1H, d, J = 7.6 Hz, naphth.), 8.13 (1H, s, $C_{10}H_6$), 8.22 (1H, m, C_6H_4), 8.30 (1H, m, C_6H_4), 8.57 (2H, br s, β-H), 8.70 (1H, d, J = 7.6 Hz, naphth.), 8.78 (4H, m, naphth.+β-H), 8.97 (2H, d, J = 4.4 Hz, β-H), 9.11 (2H, d, J = 4.4 Hz, β-H). HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{62}H_{31}F_{10}N_5O_3$, 1082.2111; found 1082.2142.

Preparation of corrole dyad 26. Aldehyde **20** (1.54 g, 3.47 mmol) and 5-(pentafluorophenyl)dipyrrane (**21**, 2.17 g, 6.95 mmol) were dissolved in 50 mL of DCM and 0.57 mL of TFA stock solution (see above) was added. The reaction mixture was stirred at rt for 20 min and then the reaction was quenched by the addition of triethylamine (0.1 mL). The reaction mixture was diluted with DCM to 450 mL and DDQ (2.05 g, 9 mmol; dissolved in minimal amount of toluene) was added. After 2 h of stirring at rt, the reaction mixture was passed through silica pad, and then chromatographed (DCM/hexanes 1:1). The product was contaminated with additional fluorescent compounds which were successfully removed by the chromatography on SEC (eluted with toluene). Product-containing fractions were collected and evaporated. After crystallization, corrole **26** was obtained as dark fine powder (211 mg, 6%). R_f 0.4 (DCM/hexanes 1:1). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^{-3}$) 429 (153), 563 (15.2), 613 (11.6), 645 (6.9). ^{1}H NMR (500 MHz, THF-d_8): δ, ppm (-4)–(-1.5) (3H, br s, NH), 6.90 (2H, br s, NH_2), 7.02–7.36 (10H, m, Ph), 7.93 (2H, d, J = 8 Hz, C_6H_4), 8.33 (2H, d, J = 8 Hz, C_6H_4), 8.63 (2H, br s, β-H), 8.71 (2H, m, β-H), 8.83 (2H, br s, β-H), 9.14 (2H, br s, β-H). HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{58}H_{28}F_{10}N_7O_2$, 1044.2139; found 1044.2171.

Preparation of 2-(p-tolyl)-benzo[f]isoindole-1,3-dione (28). Anhydride **2** (396 mg, 2 mmol) and *p*-toluidine (**27**, 214 mg, 2 mmol) were heated under reflux in 10 mL of AcOH overnight. After cooling, the resulting precipitate was filtered off and washed with AcOH and EtOH, affording 499 mg (87%) of **28** as off-white powder. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ, ppm 2.42 (3H, s, CH_3), 7.33, 7.37 (4H, AA′BB′, J = 8.3 Hz), 7.71–7.74 (2H, m, $C_{10}H_6$), 8.07–8.11 (2H, m, $C_{10}H_6$), 8.44 (2H, s, $C_{10}H_6$). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ, ppm 21.2, 125.2, 126.5, 127.5, 129.2, 129.3, 129.8, 130.3, 135.7, 138.3, 167.2. Anal. calcd. for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88; found C, 79.42; H, 4.55; N, 4.81. HRMS-ESI: *m/z* $[M + H]^+$ calcd. for $C_{19}H_{14}NO_2$, 288.1025; found 288.1028.

Preparation of 4-amino-1,3-dioxo-6,7-diphenyl-2-p-tolyl-2,3-dihydro-1H-isoindole-5-carbonitrile (29). Anhydride **19** (511 mg, 1.5 mmol) and *p*-toluidine (**27**, 193 mg, 1.8 mmol) were heated under reflux in 5 mL of AcOH overnight. After cooling, solvent was evaporated off, the residue was dissolved in chloroform, washed with $NaHCO_3$, water and brine. The organic layer was separated and dried over $MgSO_4$. Flash column chromatography (DCM/hexanes 1:3 → 2:1) and crystallization (chloroform/hexanes) afforded 350 mg (54%) of **29** as yellow crystals. R_f 0.3 (DCM/hexanes 1:2). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ, ppm 2.37 (3H, s, CH_3), 6.14 (2H, br s, NH_2), 7.01 (2H, m, C_6H_4), 7.03 (2H, m, C_6H_4), 7.11 (3H, m, Ph), 7.15 (7H, m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ, ppm 21.2, 103.7, 111.0, 115.1, 126.3, 127.6, 127.7, 128.2, 128.5, 128.8, 129.4, 129.5, 129.6, 130.4, 132.0, 133.6, 136.1, 138.2, 146.4, 153.9, 165.7, 167.8; Anal. calcd. for $C_{28}H_{19}N_3O_2$: C, 78.31; H, 4.46; N, 9.78; found C, 78.37; H, 4.44; N, 9.83. HRMS-ESI: *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{19}N_3O_2Na$, 452.1370; found 452.1392.

Spectroscopy and photophysics

Spectroscopic grade toluene (C. Erba) was used without further purification. The absorption spectra

were recorded by a Perkin-Elmer Lambda 950 UV-vis spectrophotometer and the emission spectra corrected for the photomultiplier response were detected by an Edinburgh FLSP920 fluorimeter equipped with a R928P Hamamatsu photomultiplier with a spectral coverage from 200 nm to *ca*. 820 nm. Fluorescence quantum yields, when reported, were calculated from the corrected luminescence spectra against a reference with the following Equation 1:

$$\phi_{em} = \frac{A_r n^2 I}{n_r^2 I_r A} \phi_r \quad (1)$$

The reference used for **28** emission quantum yield was air-equilibrated quinine sulphate in 1N H_2SO_4 with ϕ_{fl} = 0.546 [23], whereas the reported value of 0.14 for **30** was used as reference to calculate the emission quantum yield of the corrole units [12a].

Fluorescence lifetimes in the nanosecond region were detected by a Time Correlated Single Photon Counting apparatus (IBH) with excitation at 331 or 465 nm. A system based on a Streak Camera Hamamatsu C1587 equipped with M1952 and a Nd-YAG laser (Continuum PY62/10, 35 ps pulse, 1 mJ at 355 nm) was used for detecting luminescence with picosecond resolution [24]. Estimated errors are 10% on lifetimes, molar extinction coefficients and quantum yields. The working temperature, if not otherwise specified, is 295 ± 2 K.

CONCLUSION

The comparison of three different methodologies leading to various small aromatic imides bearing formyl groups has proven that both reaction with commercially available polymers of aminobenzaldehydes and utilization of aminobenzyl alcohols are the best strategies in terms of overall efficiency. We proved that regardless the orientation of naphthalene-2,3-imide moiety *vs*. corrole ring the interaction between these chromophores is small. Still placing it above the corrole ring induces small changes in photophysical behavior. We also have shown that while altering the size and electron density in blue-absorbing aromatic imides one can manipulate the behavior of bichromophoric systems. While large, slightly polarized imides tend to lead to energy transfer, small and strongly polarized derivatives of phthalimide induced more complex behavior.

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REFERENCES

1. Balzani V, Ceroni P and Juris A. *Photochemistry and Photophysics: Concepts, Research, Applications*, Wiley-VCH: 2014.
2. Scholes GD, Fleming GR, Olaya-Castro A and van Grondelle R. *Nat. Chem.* 2011; **3**: 763–774.
3. Andreiadis ES, Chavarot-Kerlidou M, Fontecave M and Artero V. *Photochem. Photobiol.* 2011; **87**: 946–964.
4. Gust D and Moore TA. In *The Porphyrin Handbook*, *Electron Transfer*, Vol. 8, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: 1999; pp 153–184.
5. Ohkubo K, Kotani H, Shao J, Ou Z, Kadish KM, Li G, Pandey RK, Fujitsuka M, Ito O, Imahori H and Fukuzumi S. *Angew. Chem., In. Ed.* 2004; **43**: 853–856.
6. (a) Bottari G, de la Torre G, Guldi DM and Torres T. *Chem. Rev.* 2010; **110**: 6768–6816. (b) Göransson E, Boixel J, Fortage J, Jacquemin D, Becker H-C, Blart E, Hammarström L and Odobel F. *Inorg. Chem.* 2012; **51**: 11500–11512.
7. (a) Oh J, Sung J, Kitano M, Inokuma Y and Osuka A. Kim D. *Chem. Commun.* 2014; **50**: 10424–10426. (b) Osuka A, Tsurumaki E and Tanaka T. *Bull. Chem. Soc. Jpn.* 2011; **84**: 679–697.
8. (a) Flamigni L, Ventura B, Tasior M and Gryko DT. *Inorg. Chim. Acta* 2007; **360**: 803–813. (b) Tasior M, Gryko DT, Cembor M, Jaworski JS, Ventura B and Flamigni L. *New J. Chem*. 2007; **31**: 247–259. (c) Flamigni L, Ventura B, Tasior M, Becherer T, Langhals H and Gryko DT. *Chem. Eur. J*. 2008; **14**: 169–183. (d) Gros CP, Brisach F, Meristoudi A, Espinoza E, Guilard R and Harvey PD. *Inorg. Chem*. 2007; **46**: 125–135. (e) Tasior M, Gryko DT, Shen J, Kadish KM, Becherer T, Langhals H, Ventura B and Flamigni L. *J. Phys. Chem. C* 2008; **112**: 19699–19709. (f) D'Souza F, Chitta R, Ohkubo K, Tasior M, Subbaiyan NK, Zandler ME, Rogacki MK, Gryko DT and Fukuzumi S. *J. Am. Chem. Soc.* 2008; **130**: 14263–14272. (g) Tasior M, Gryko DT, Pielacińska DJ, Zanelli A and Flamigni L. *Chem. Asian J*. 2010; **1**: 130–140. (h) Tasior M, Voloshchuk R, Poronik YM, Rowicki T and Gryko DT. *J. Porphyrins Phthalocyanines* 2011; **15**: 1011–1023. (i) Ciuciu AI, Flamigni L, Voloshchuk R and Gryko DT. *Chem. Asian J*. 2013; **8**: 1004–1014. (j) Voloshchuk R, Gryko DT, Chotkowski M, Ciuciu AI and Flamigni L. *Chem. Eur. J*. 2012; **18**: 14845–14859. (k) Flamigni L, Ciuciu AI, Langhals H, Böck B

and Gryko DT. *Chem. Asian J*. 2012; **7**: 582–592. (l) Flamigni L and Gryko DT. *Chem. Soc. Rev*. 2009; **38**: 1635–1646. (m) Flamigni L, Vyrostek D, Voloshchuk R and Gryko DT. *Phys Chem. Chem. Phys.* 2010; **12**: 474–483.

9. (a) Paolesse R. In *The Porphyrin Handbook*, Vol. 2, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: San Diego, CA, 2000; pp 201. (b) Sessler JL and Weghorn SJ. In *Expanded, Contracted & Isomeric Porphyrins*, Pergamon: Oxford, 1997; pp 11. (c) Erben C,Will S and Kadish KM. In *The Porphyrin Handbook*, Vol. 2, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: San Diego, CA, 2000; pp 233. (d) Montforts F-P, Glasenapp-Breiling M and Kusch D. In *Houben-Weyl Methods of Organic Chemistry*, Vol E9d, Schaumann E. (Ed.) Thieme: Stuttgart, New York, 1998; pp 665–672. (e) Gryko DT. *Eur. J. Org. Chem.* 2002; 1735–1743. (f) Guilard R, Kadish KM, Barbe J-M and Stern C. In *The Porphyrin Handbook*, Vol 18, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: 2003; pp 303–351. (g) Gryko DT, Fox JP and Goldberg DP. *J. Porphyrins Phthalocyanines* 2004; **8**: 1091–1105. (h) Nardis S, Monti D and Paolesse R. *Mini-Rev. Org. Chem.* 2005; **2**: 355–372. (i) Goldberg DP. *Acc. Chem. Res.* 2007; **40**: 626–634. (j) Aviv I and Gross Z. *Chem. Commun.* 2007; 1987–1999. (k) Johnson AW and Kay IT. *Proc. Chem. Soc. London* 1964; 89–90.
10. (a) Gross Z, Galili N and Saltsman I. *Angew. Chem. Int. Ed.* 1999; **38**: 1427–1429. (b) Paolesse R, Nardis S, Sagone F and Khoury RM. *J. Org. Chem.* 2001; **66**: 550–556. (c) Briñas RP and Brückner C. *Synlett* 2001; 442–444. (d) Gryko DT and Jadach K. *J. Org. Chem.* 2001; **66**: 4267–4275. (e) Sakow D, Böker B, Brandhorst K, Burghaus O and Bröring M. *Angew. Chem. Int. Ed.* 2013; **52**: 4912–4915. (f) Gryko DT, Tasior M and Koszarna B. *J. Porphyrins Phthalocyanines* 2003; **7**: 239–248. (g) Geier GR III, Chick JFB, Callinan JB, Reid CG and Auguscinski WP. *J. Org. Chem.* 2004; **69**: 4159–4169. (h) Jeandon C, Ruppert R and Callot HJ. *Chem. Commun.* 2004; 1090–1091. (i) Koszarna B and Gryko DT. *J. Org. Chem.* 2006; **71**: 3707–3717. (j) Gryko DT and Koszarna B. *Synthesis* 2004; 2205–2209. (k) Stefanelli M, Nardis S, Tortora L, Fronczek FR, Smith KM, Licoccia S and Paolesse R. *Chem. Commun*. 2011; **47**: 4255–4257. (l) Tortora L, Nardis S, Fronczek FR, Smith KM and Paolesse R. *Chem. Commun*. 2011; **47**: 4243–4245. (m) Barata JFB, Silva AMG, Neves MGPMS, Tomé AC, Silva AMS and Cavaleiro JAS. *Tetrahedron Lett*. 2006; **47**: 8171–8174.
11. (a) Kupershmidt L, Okun Z, Amit T, Mandel S, Saltsman I, Mahammed A, Bar-Am O, Gross Z and Youdim MBH. *J. Neurochem.* 2010; **113**: 363–373. (b) Kanamori A, Catrinescu M-M, Mahammed A, Gross Z and Levin LA. *J. Neurochem.* 2010; **114**: 488–498.
12. (a) Ventura B, Degli Esposti A, Koszarna B, Gryko DT and Flamigni L. *New J. Chem*. 2005; **29**: 1559–1566. (b) Ding T, Alemán EA, Mordarelli DA and Ziegler CJ. *J. Phys. Chem. A* 2005; **109**: 7411–7417. (c) Kowalska D, Liu X, Tripathy U, Mahammed A, Gross Z, Hirayama S and Steer RP. *Inorg. Chem.* 2009; **48**: 2670–2676.
13. Shao J, Shen J, Z Ou, Wenbo E, Koszarna B, Gryko DT and Kadish KM. *Inorg. Chem*. 2006; **45**: 2251–2265.
14. (a) Wallin S, Monnereau C, Blart E, Gankou J-R, Odobel F and Hammarström L. *J. Phys. Chem. A* 2010; **114**: 1709–1721. (b) Miller SE, Lukas AS, Marsh E, Bushard P and Wasielewski MR. *J. Am. Chem. Soc.* 2000; **122**: 7802–7810.
15. (a) Röger C, Miloslavina Y, Brunner D, Holzwarth AR and Würthner F. *J. Am. Chem. Soc*. 2008; **130**: 5929–5939. (b) Gunderson VL, Smeigh AL, Hoon Kim C, Co DT and Wasielewski MR. *J. Am. Chem. Soc.* 2012; **134**: 4363–4372. (c) Guha S, Goodson FS, Roy S, Corson LJ, Gravenmier CA and Saha S. *J. Am. Chem. Soc.* 2011; **133**: 15256–15259.
16. (a) De Mico A, Margarita M, Parlanti M, Vescovi A and Piancatelli G. *J. Org. Chem.* 1997; **62**: 6974–6977. (b) Nowak–Król A, Koszarna B, Yoo SY, Chromiński J, Węcławski MK, Lee C-H and Gryko DT. *J. Org. Chem.* 2011; **76**: 2627–2634.
17. Lukas AS, Bushard PJ, Weiss EA and Wasielewski MR. *J. Am. Chem. Soc.* 2003; **125**: 3921–3930.
18. Gewald K. *Chem. Ber.* 1996; **99**: 1002–1007.
19. Flamigni L, Ventura B, You C-C, Hippius C and Würthner F. *J. Phys. Chem. C*. 2007; **111**: 622–630.
20. Armarego WLF and Chai CLL. *Purification of Laboratory Chemicals* (4th edn), Elsevier Science: 2003.
21. Imahori H, Azuma T, Ozawa S, Yamada H, Ajavakom A, Norieda H, Sakata Y and Ushida K. *Chem. Commun.* 1999; **35**: 557–558.
22. Clayden J, Pickworth M and Jones LH. *Chem. Commun.* 2009; **45**: 547–549.
23. Eaton DF. *Pure Appl. Chem.* 1988; **60**: 1107–1114.
24. Flamigni L, Talarico AM, Chambron JC, Heitz V, Linke M, Fujita N and Sauvage J-P. *Chem. Eur. J.* 2004; **1**: 2689–2699.