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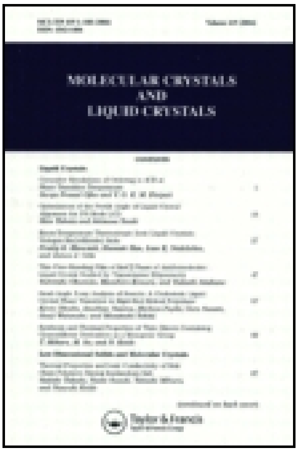

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Corrole-Fullerene Dyads: Will They Replace Porphyrin-Fullerene Systems?

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Available online: 12 Jan 2012

To cite this article: Andrzej Graja (2012): Corrole-Fullerene Dyads: Will They Replace Porphyrin-Fullerene Systems?, Molecular Crystals and Liquid Crystals, 554:1, 31-42

To link to this article: http://dx.doi.org/10.1080/15421406.2012.632744

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Mol. Cryst. Liq. Cryst., Vol. 554: pp. 31–42, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.632744

Corrole-Fullerene Dyads: Will They Replace Porphyrin-Fullerene Systems?

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A short review of the unique spectral properties of corroles—new members of porphines—is given. Main physical properties of corroles and their covalent dyads with fullerene are presented and discussed. A comparison of corroles properties with those of similar systems containing porphyrins is also given. Some advantages and disadvantages of the corrole-fullerene systems are bring into relief.

Keywords Corrole; fullerene; porphyrin; UV-Vis-IR spectroscopy

1. Introduction

One of the most important and interesting chemical reactions in nature is conversion of sunlight into chemical potential in photosynthesis [1–5]. The physical reason of this effect is photoinduced electron transfer in the photosynthetic reaction centre. Photosynthesis has been widely investigated not only for understanding all aspects of this fascinating process but also because of its potential applications [6]. Organic solar cells are the most promising devices taking advantages of this effect. For designing efficient artificial photoactive devices there are certain requirements that must be met: 1) light must be captured by molecules leading to excited states, 2) absorption of light must result in the transfer of an electron to an acceptor, 3) the electron transfer must be directional, and 4) the lifetimes of the excited states must be long enough for electron transfer to take place [7,8]. Organic solar cells containing fullerene C_{60} as an electron acceptor and organic dye as a chromophore (electron donor) fulfill these requirements and exhibit a high potential for production of efficient and low-cost photovoltaic devices [3,9]. The excellent electron-accepting capability of fullerenes makes them appropriate building blocks for organic solar cells designing [10]. On the other hand, porphyrin-derived dyes are perfect and commonly used chromophores in solar cells. Among various porphyrin-derived dyes corroles are most widely discussed in the paper.

In this review I would like to describe the recent developments in the studies of photoinduced electron transfer in the molecular systems of the type fullerene-porphyrin-derived chromophore. The physical basis of the photoinduced electron transfer as well as typical photoactive porphyrin-derived materials are also summarized.

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2. Porphyrins and Corroles—What are They?

Heterocyclic dyes are the most frequently employed building blocks as electron donors and sensitizers in artificial photosynthetic systems. Among them porphyrin and porphyrin-like molecules play a crucial role. Porphyrins are macrocycles composed of four modified pyrrole subunits interconnected at their carbon atoms *via* methine bridges (=CH−) (Fig. 1a). Differences in properties of substituted porphyrins come from perturbations of energy states due to the presence of metal, substituents or peripheries of the conjugated ring systems, the number and type of ligands, solvent properties, degree of aggregation and architecture of the molecule [11,12]. Porphyrins are characterized by strong absorption bands at about 420–450 nm (Soret region) with high absorption coefficient of the order

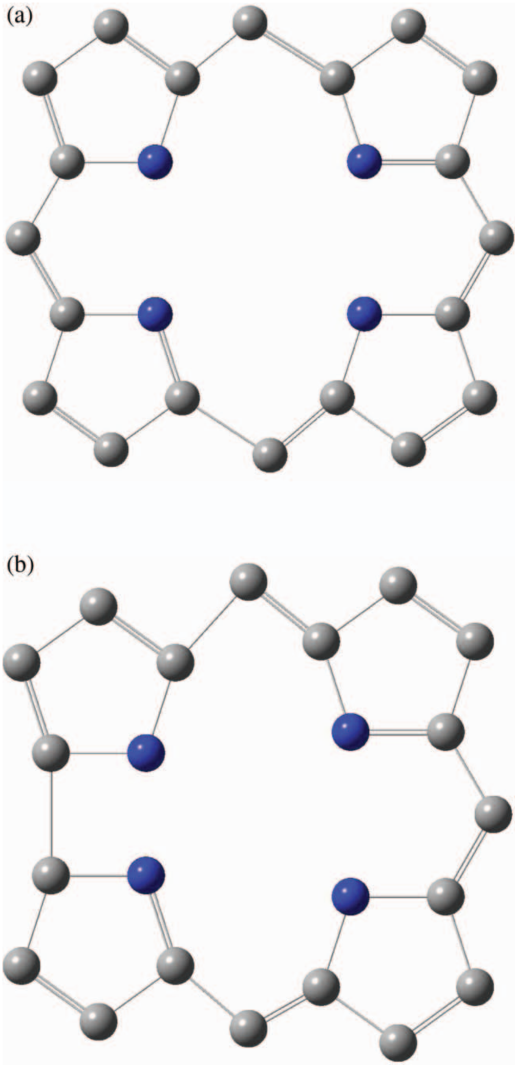

Figure 1. Molecular structure of free base parent porphyrin, (a) and free base parent corrole (b); grey spheres represent carbon atoms, blue spheres—nitrogen atoms.

of 10^5 cm^{-1} and much less intense Q bands in the long wavelength region 500–650 nm (Fig. 2a). Most of the porphyrin dyes show intensive fluorescence in the range 600–800 nm (Fig. 2b). The fluorescence lifetime values of many porphyrins range from about 10^{-9} to $1.5\cdot10^{-8}$ s with the corresponding fluorescence quantum yields of 1% to above 15% (e.g. chlorophylls) [11,12].

Corroles (Fig. 1b) are one-carbon-shorter analogues of porphyrins possessing the skeleton of corrin with three *meso*-carbons between the four pyrrole rings [13]. When compared with porphyrins, these tribasic aromatic macrocycles exhibit lower oxidation potentials, higher fluorescence quantum yields, larger Stokes shifts, and more intense absorption of red light [14,15]. Free-base corroles reveal the Soret-type absorption (Fig. 2a) in the 400–440 nm region ($\varepsilon \approx 120{,}000$ m^2/mol, where ε is the molar extinction coefficient) and the Q band transitions between 500 and 700 nm ($\varepsilon \approx 10{,}000$–$20{,}000$ m^2/mol in free base corroles and about 20,000–40,000 m^2/mol in metalated ones). Absorption spectra of corroles exhibit two important differences from those of porphyrins. Firstly, there is a greater change in the optical absorption of the corroles upon variation of the substitution on the phenyl group than in the corresponding porphyrins. Secondly, corroles exhibit very significant solvent-dependent absorbance and absorption band shape in contrast to the small changes typically detected in porphyrins [16]. Fluorescence spectra (Fig. 2b) of corroles are characterized by strong emission bands between 620 and 680 nm with fluorescence quantum yield 2–30% depending on substituents and solvents [13–16]. The luminescence lifetime is of the order of a few nanoseconds. The fluorescence quantum yields of the substituted corroles are in general higher than those of the analogous porphyrins [16]. In addition, the effect of substituents on the optical properties of corroles is significantly larger than in porphyrins. Study of electrochemistry of free-base *meso*-substituted corroles gives their first oxidation potential in benzonitrile in the range 0.38–0.87 V. Corroles are, in general, less stable than porphyrins but the stability of dyads are better than that of the corresponding component corrole.

3. Photoinduced Electron Transfer

Roughly speaking, the process of converting light into electric current in an organic photovoltaic cell is accomplished by four consecutive steps [17]:

Firstly, absorption of a photon leading to formation of an excited state, the electron-hole pair or exciton,

Secondly, exciton diffusion to the donor-acceptor region, where the charge separation occurs,

Thirdly, charge separation, resulting in the appearance of holes in the donor and electrons in the acceptor,

Fourthly, charge transport of the holes to an anode and the electrons to a cathode in order to supply a direct current for the load.

These processes are schematically shown in Fig. 3. Intermolecular photoinduced electron transfer (ET) is a process in which an electron is transferred from an electron-donating species (D) to an electron-accepting one (A), producing the radical cation of the donor (D^{+}) and the radical anion of the acceptor (A^{-}). Photoactive organic systems should display intense and broad absorption bands over a wide wavelength range. In the case of solar cells the absorption should lead to efficient light harvesting in active layers. A critical factor in photoinduced ET lies in the matching of D and A with suitable electrochemical and photophysical properties [18]. Knowledge of the excited state energies of the chromophores and

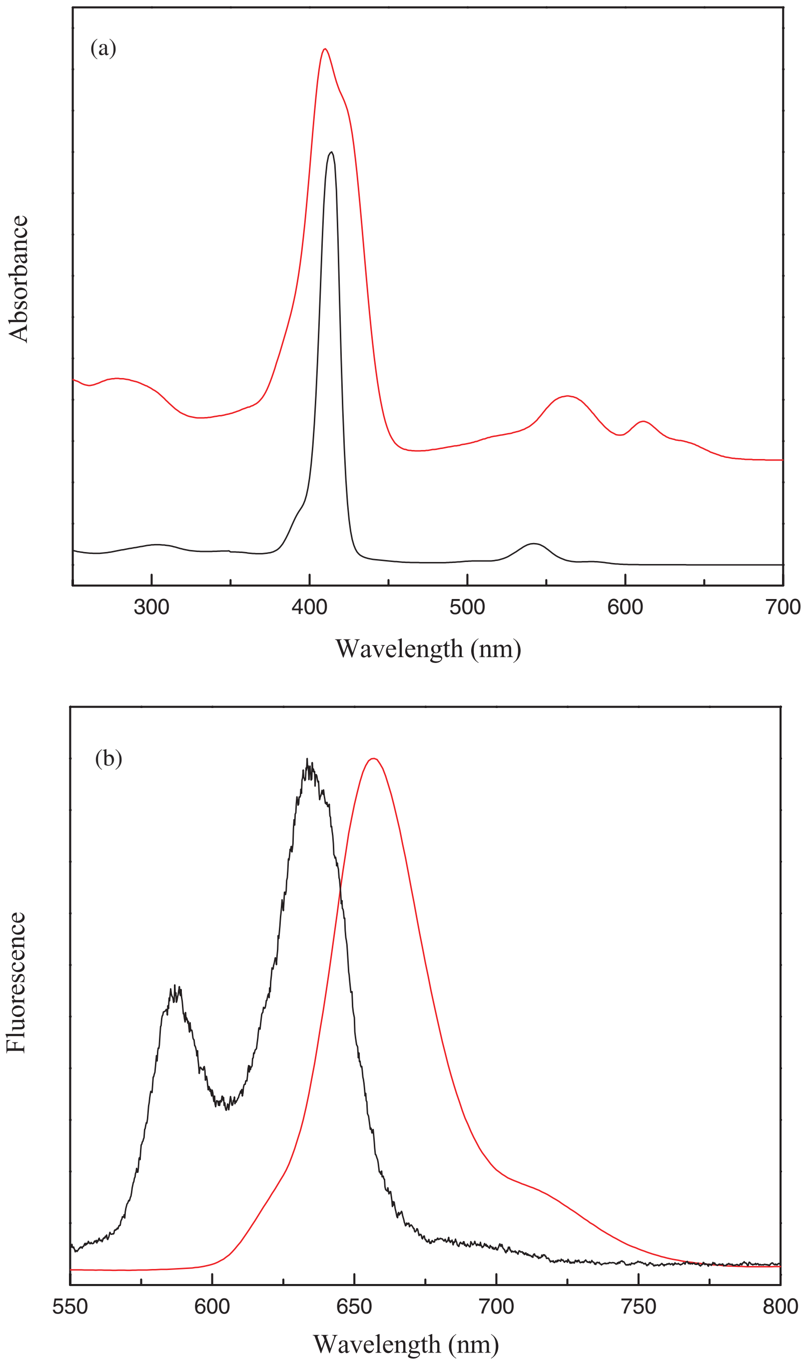

Figure 2. Electronic absorption (a) and fluorescence (b) spectra of zinc porphyrin (red line) and *meso*-pentafluorophenyl corrole (black line), both in aprotic solvent.

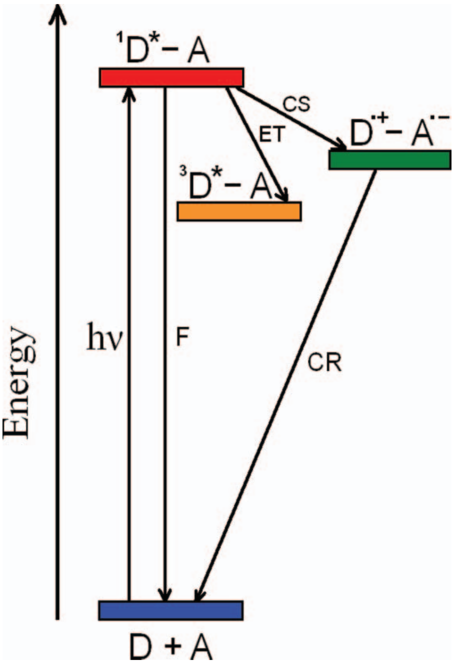

Figure 3. Schematic energy diagram showing photoinduced electron transfer (ET), charge separation (CS) and charge recombination (CR) processes as well as fluorescence (F) in a photoactive donor-acceptor (D-A) system.

the redox potentials of D and A is thus an essential requirement to investigate photoinduced ET. These requirements are relatively good fulfilled for commonly investigated porphyrin-fullerene systems [2–5,7,19,20]. These types of systems mimic natural photosynthetic processes.

To generate negative- and positive-charged carriers, the excitation needs to migrate to the donor-acceptor interface, where they can dissociate. The excitons diffuse randomly and they need to reach the heterojunction between the D and A molecules prior to their decay back to the ground state. Hence, the thickness of the organic layer should be comparable to the exciton diffusion length λ, where $\lambda = (\delta\tau)^{1/2}$; δ is the diffusion coefficient and τ is the lifetime of the exciton [21].

Upon reaching the donor-acceptor interface, excitons dissociate into electrons and holes. Exciton dissociation is a two-step process. Initially, an exciton state at the interface evolves into a charge-transfer (CT) state D^+-A^- and then it either recombinants to the ground state or dissociates into free carriers *via* charge-separated (CS) states. The energy (E) of the CT state is defined by the ionization potential I_d of the donor and electron affinity E_a of the acceptor. On the other hand, E can be roughly approximated by the difference between the HOMO and LUMO energies of the donor and acceptor. Efficiency of energy conversion depends on the relative time scales of internal conversion (IC), expressed by the IC rate constant k_{IC}, and CS rate constant k_{CS}. If $k_{IC} \gg k_{CS}$ the exciton evolve into the CT state which undergoes a fast relaxation to its lowest electronic or vibrational state. To dissociate, the electron and hole need to overcome the Coulomb barrier. Thus, the exciton dissociation *via* this pathway is not likely to be an efficient process. Contrary to this case, if $k_{IC} \ll k_{CS}$ exciton dissociation can take place *via* excited levels of the CT or CS states.

The formation of CT or CS states can be extremely fast; as a result many internal relaxation processes are much slower than these CT or CS rates. The CT states formed *via* exciton dissociation display lifetimes about two orders of magnitude shorter than those of the CT states formed directly from the ground state. As a result, the sub-gap CT excitations contribute less to the device photovoltaic response [3–5,7,21].

Once the charges are separated, they move toward their respective electrodes with an efficiency depending upon their mobilities. Unfortunately, in organic materials, the weakness of the electronic coupling, the large electron-vibration coupling and the disorder effects conspire to produce modest carrier mobilities. The charge-carrier mobilities strongly depend on sample morphology and can vary over several orders of magnitude when going from highly disordered amorphous films (10^{-6}–10^{-3} $cm^2\ V^{-1}s^{-1}$) to highly ordered materials (>1 $cm^2\ V^{-1}s^{-1}$).

Concluding these remarks we stress that the optimization of organic solar cells requires a fine balancing of all processes occurring in photoactive organic systems. It is necessary to find an optimal compromise among the material characteristics that can work in opposite directions. In particular, the optimization of the D/A interface can increase the electronic coupling between the charge transfer or charge separation and electronic states, thereby enhancing the photocurrent but, can also increase the coupling between the CT states and the D/A ground state, leading to a larger reverse saturation current in the dark, which should be minimized to secure a higher open-circuit voltage [3,7,18–21]. Thus, designing organic photovoltaic devices one must find careful balances and a comprehensive understanding of all the processes that occur in such systems.

4. Photoactive Corrole-Based Dyads

A critical factor in the photoinduced electron transfer lies in the successful matching of D and A with suitable electrochemical and photophysical properties for the occurrence of an exothermic electron transfer. In the majority of donor-fullerene linked systems designed with the use of symmetric tetrapyrroles such as porphyrins or phthalocyanines, it was difficult to probe a slower charge recombination process. Thus, it is desired to develop donor-acceptor dyads which can afford the long-lived charge-separated states [13,22]. One possibility is to replace these symmetric donors with *e.g.* corroles [23].

The first example of covalently linked free-base corrole-fullerene dyads was reported by D’Souza et al. [13]. The authors have synthesized series of donor-acceptor dyads linked together by a phenyl or a biphenyl spacer unit. The corrole containing two *meso*-pentafluorophenyl entities was used as a donor. These corrole substituents stabilize the corrole macrocycle and being electron-withdrawing, they suitably position the energy level of the charge-separated state to achieve long-lived radical ion-pairs [13]. Corrole-fullerene dyads studied by D’Souza et al. reveal an absorption band at around 310 nm [13]. The Soret band of the dyad is blue-shifted by 5 nm compared to the reference corrole; such a trend is also observed for the Q bands around 560 nm. These shifts suggest electronic interactions between the corrole and fullerene entities of the dyad. The HOMO state of the dyad is located mainly on the corrole π-system, but the part of HOMO is also on a spacer of the dyad. The LUMO state is placed on the fullerene spheroid [13,24]. The locations of HOMO and LUMO suggest formation of the corrole$^+$-fullerene$^-$ charge-separated state during photoinduced electron transfer [13]. Free-base corroles reveal an emission band at 656 nm with a shoulder around 714 nm but in the dyad this emission is fully quenched [25]. Luminescence quenching was characterized by the rates of the order of 10^9–10^{11} s^{-1} [13]. This result indicates efficient excited-state events in the dyad. The rate constant of charge separation (k_{CS}) is between 10^{10} and 10^{11} s^{-1}, the quantum yield (ϕ_{CS}) is found to be >97% but the lifetime of the radical ion-pair (τ_{RIP}) is between 10^{-11} and 10^{-6} s depending on the polarizability of used solvent [13]; it suggests an efficient photoinduced electron transfer process.

Free-base porphyrin-free-base corrole dyad connected by an amide linkage was synthesized and characterized by the Italian-Polish team [26]. Though the absorption spectra of the two tetrapyrrole components were overlapping, it was possible to excite one of the chromophores at selective wavelengths, at 570 nm (corrole) and 515 nm (porphyrin). Results obtained from time resolved and steady state spectroscopy experiments indicate the existence of an equilibrium between the two lowest singlet excited states of the dyad, one localized on the corrole and one on the porphyrin unit, which are nearly isoenergetic ($\Delta G = -0.01$ eV). Independently of the excited component, energy transfer occurs in both directions with the equilibrium constant k_{cq} close to 1, and it is rapidly sets with back and forward rates of the order of 10^9 s^{-1}. Both states decay with the common lifetime of $6.2 \cdot 10^{-9}$ s; that is longer compared to that of corrole ($3.9 \cdot 10^{-9}$ s) and shorter with respect to that of porphyrin ($9.9 \cdot 10^{-9}$ s). The longer lived excited state localized on porphyrin acts as a reservoir for the excited state localized on corrole. The energy levels of the excited singlet state of the component units are very similar, of the order of 1.9 eV, justifying interpretation of equilibration between the populations of the two excited states at room temperature [26]. According to authors of the paper [26] the deactivation occurs through the shorter lived corrole but the porphyrin excited state acts as a reservoir of energy, extending the lifetime of the emitter. In the case of a system in equilibrium, the observed rate constants are combinations of those of the individual steps and in this case a complete kinetic analysis of the system was provided [26]. The energy transfer rate from corrole excited singlet to porphyrin and the reverse energy transfer from porphyrin to corrole resulted in good agreement with the energy transfer rates calculated according to the Förster mechanism [27].

5. Vibrational Spectra of Corroles

According to our knowledge a first systematic spectral studies of substituent effects in metallocorroles were performed by Ghosh et al. [28]. The authors have recorded and analyzed the electronic and infrared (IR) absorptions and resonance Raman (RR) scattering of ten copper(III) *meso*-triarylcorroles. Shortly speaking, the authors [28] have observed that both IR and RR show two and possibly more high-frequency bands in the 1400–1550 cm^{-1} region exhibiting significant frequency downshifts on β-octabromination, thus qualifying them as structure-sensitive marker bands. Geometry optimizations with the density functional theory (DFT) indicate that the saddled conformation should be clearly preferred for the β-octabromo-*meso*-triarylcorrole derivatives and that β-octabromination results in expansion of a number of skeletal bond distances of the corrole macrocycle, consistent with the observed frequency downshifts [28]. Soret-resonant Raman spectra of planar and nonplanar Cu(III) *meso*-triarylcorroles show that the frequencies of a number of skeleton vibrations downshift significantly in the nonplanar corroles, relative to the planar analogues, in a manner that is exactly analogous to behavior of the RR marker bands of metalloporphyrines [29]. Thus, the frequencies of the "marker bands" can furnish information on such issues as the core size of metallocorroles, the degree of saddling or ruffling in the case of nonplanar corroles, and whether the corrole ligand is innocent or has radical character analogous to the metalloporphyrins.

UV-vis, IR, and RR spectra of high-valent molybdenum(V)-oxo complex of 5,10,15-tris[3,5-bis(trifluoromethyl)phenyl]corrole were studied by Czernuszewicz et al. [30]. The key vibrational mode, $\nu(\mathrm{Mo^VO})$, was identified in both the solid state and solution by ^{18}O-isotope labeling of the terminal oxo ligand. This stretching vibration in the solid state sample was recorded at 969 $\mathrm{cm^{-1}}$. It was strongly enhanced in resonance with the Soret electronic transition, and its frequency was sensitive to solute-solvent interactions; it shifts to 975 $\mathrm{cm^{-1}}$ in hexane and then gradually shifts to lower frequencies in more polar solvents, down to 960 $\mathrm{cm^{-1}}$ in dimethyl sulfoxide. It was also shown, that the $\nu(\mathrm{Mo^VO})$ frequency, recorded in 25 aprotic solvents, decreases in proportion to a solvent polarity parameter ($A + B$) of Swain et al. [31], (where A and B are the solvent's acidity or basicity, respectively) [30].

Recently, Czernuszewicz et al. [32] performed investigations of high-valent oxochromium(IV,V) corroles with RR spectroscopy. The Soret-excited RR spectrum of the oxochromium(V) complex of tris(pentafluorophenyl)corrole displayed a rich array of distinctive metallocorrole vibrational bands in the 900–1600 $\mathrm{cm^{-1}}$ region, with the strongest polarized features at 986, 1080, 1372, 1507, 1545, and 1582 $\mathrm{cm^{-1}}$ [30,32]. The polarized band at 986 $\mathrm{cm^{-1}}$ is due to the stretching mode of the perchromyl bond, $\nu(\mathrm{Cr^VO})$.

Just recently, Barszcz [33] have performed DFT calculations of the molecular structure as well as normal IR and Raman vibrations of metal free corrole (**1**) and adequate porphyrin (**2**), shown in Fig. 4. Looking at the molecular structure of the molecules under discussion, the difference between them seems to be trivial. There is only one altered bond in the structure, the rest is identical. One can expect that between the spectra of **1** and **2** only minor differences related to the vibrations of mentioned bonds will be observed, but this is not exactly the case. This altered bond changes distinctly the macrocycle configuration (Fig. 4b,d). The central cycle of **2** is flat and two aryl groups are equally inclined in relation to the plane of the central ring. In contradiction to **2**, in the molecule **1** the central cycle is twisted but the aryl substituents are inclined in adverse side. These differences in the molecule configurations influence obviously the vibrational spectra of them [33].

The calculated IR spectra of **1** and **2** molecules (Fig. 5) are very similar one to each other. One can observe a few distinct and strong bands related to the adequate modes of vibrations in two molecules. On the other hand, the calculated Raman scattering spectra of **1** and **2** (Fig. 6) shows more differences. Only the N—H and C—H stretching modes are almost identical in both cases (about 3600 and 3200 $\mathrm{cm^{-1}}$, respectively). However, one can see the differences in intensities of their components [33]. Full description of **1** and **2** spectra and band attribution will be published soon. According to my best knowledge the assignment of the IR and Raman bands performed by Barszcz [33] is the only existing—no similar calculations and comparisons between vibrational spectra of corroles and porphyrins are known in literature.

The intramolecular and skeletal vibrations in the range of infrared spectroscopy, in particular between 1000 and 1700 $\mathrm{cm^{-1}}$ are a rich source of information on many detailed aspects of the structure and dynamics of porphyrins and corroles. The frequencies of these vibrations and the shape of the relevant bands can furnish information on such issues as: i) normal intramolecular vibrations, ii) core size of the molecule, iii) degree of saddling or ruffling in the case of nonplanar molecules, and iv) whether the ligand is innocent or has radical character. All these spectral quantities can be changed depending on environment, bonding and intermolecular interactions. For that reason the infrared and Raman spectral investigations play fundamental role in molecular studies of new functional materials.

6. Concluding Remarks

As it was mentioned at the beginning for designing efficient photoactive devices there are certain requirements that must be met. A question is: do corroles fulfill these requirements?

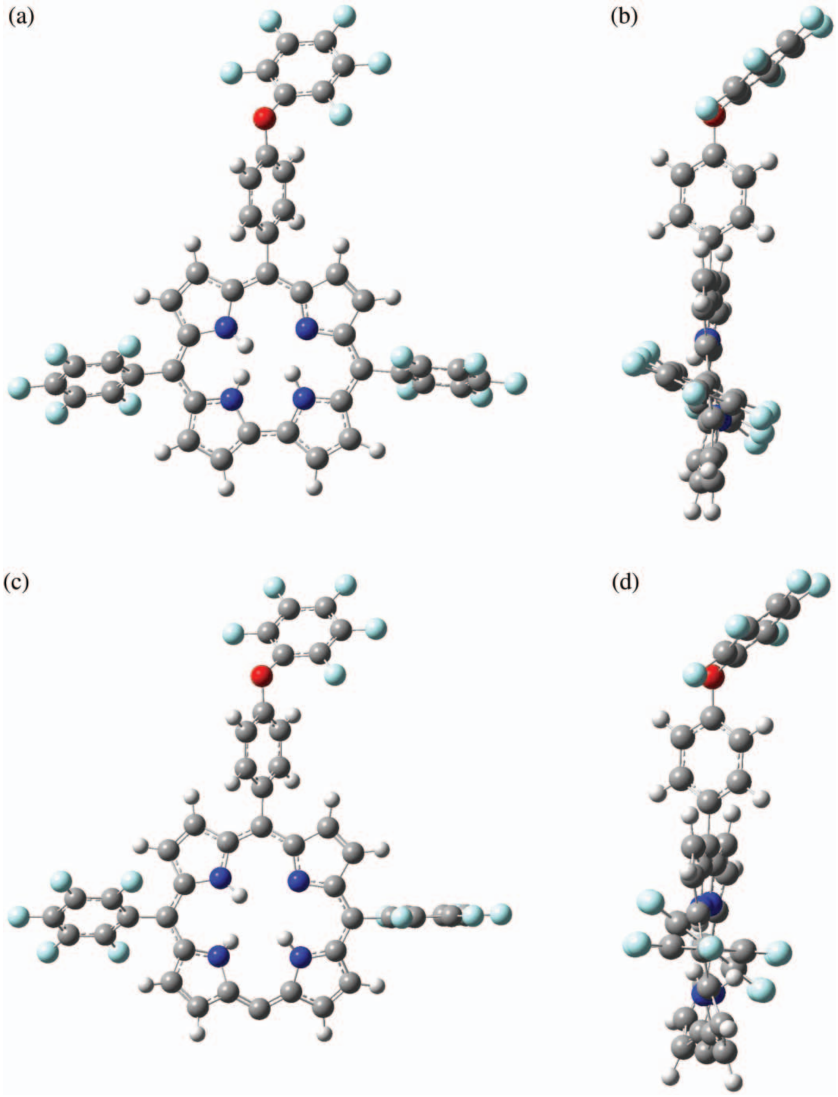

Figure 4. Molecular structure of metal free corrole, **1** (a, b) and adequate porphyrin, **2** (c, d) studied by Barszcz [33]; two projections of the molecules are shown (a-d); colored spheres represent carbon (black), hydrogen (grey), nitrogen (blue), oxygen (red), and fluorine (turquoise) atoms.

Tacking into consideration above quoted basic information on the photophysical properties of various corroles an answer is: yes! This large and constantly enlarged group of organic chromophores seems to be even more promising than porphyrins. Corroles show several superior properties with respect to those of porphyrins [14,16,22].

Corroles are, in general less stable than porphyrins but the stability of corrole dyads are better than that of the component corrole. Corroles exhibit lower oxidation potentials, higher fluorescence quantum yields, larger Stokes shifts, and more intense absorption of red light when compared with porphyrins [13–16,22]. The absorption spectra of corroles exhibit two important differences from those of porphyrins. Firstly, there is a greater

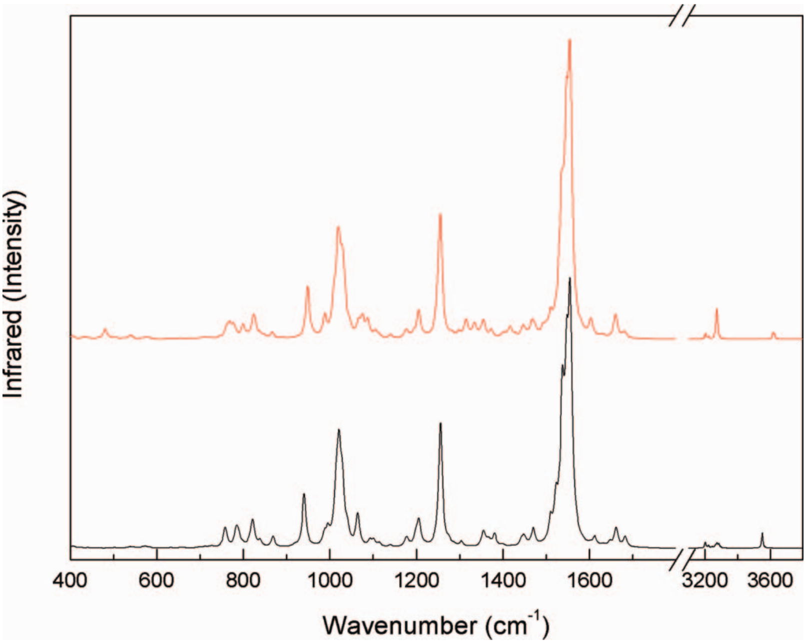

Figure 5. Calculated IR spectra of metal free-base corrole, **1** (red line) and adequate free-base porphyrin, **2** (black line) [33].

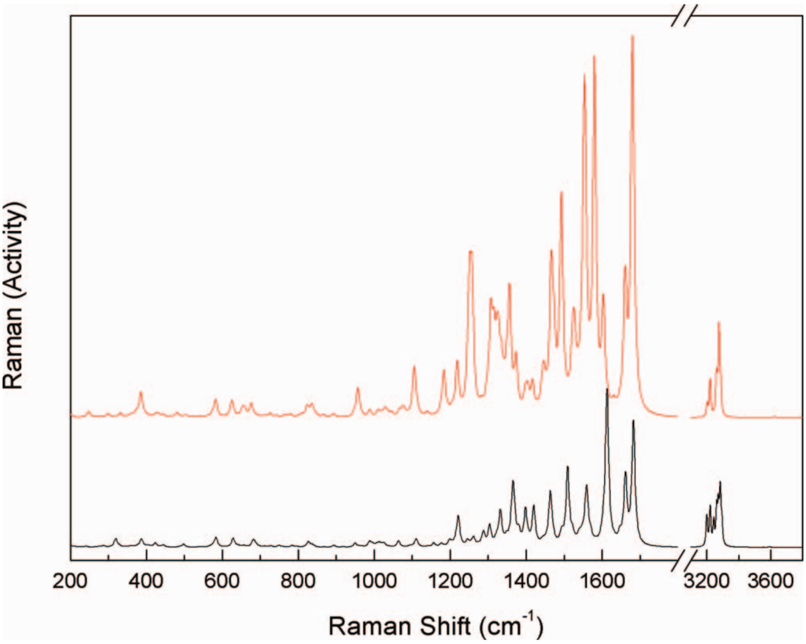

Figure 6. Calculated Raman spectra of metal free-base corrole, **1** (red line) and adequate free-base porphyrin, **2** (black line) [33].

change in the optical absorption of the corroles upon variation of the substitution on the phenyl group than in the corresponding porphyrins and secondly, corroles exhibit very significant solvent-dependent absorptions in contrast to the small effect typically detected in porphyrins [16]. The fluorescence quantum yields of the substituted corroles are in general higher than those of the analogous porphyrins [16]. Luminescence quenching of corroles is characterized by rates of the order of 10^9–10^{11} s^{-1} [13]. This result indicates efficient excited-state events in the dyad. The rate constant of charge separation (k_{CS}) is between 10^{10} and 10^{11} s^{-1}, the quantum yield (ϕ_{CS}) is found to be >97% but the lifetime of the radical ion-pair (τ_{RIP}) is between 0.04 and 6300 ns depending on polarizability of the used solvent [13]; it suggests an efficient photoinduced electron transfer process. The locations of HOMO and LUMO suggest formation of corrole$^+$-fullerene$^-$ charge-separated state during photoinduced electron transfer [13].

Corroles may act both as photosensitizers and as electron or energy relays [22]. Physical, and in particular photophysical properties of corroles allowed for their applications in various fields. There are several examples for corrole-based catalysis [34]. Corroles are capable of selectively bind various gases—this selectivity could allow for utilization of corroles as gas or the pH sensors. Corroles could be excellent candidates for active materials for the construction of electrodes. Since the corrole frontier orbitals are at higher energy than those of analogous porphyrins, their application as sensitizers in solar cells was examined [22,34,35]; this application of corroles are of great promise. There are also some medicine-oriented research of corrole-derived systems [34,36].

Acknowledgements

My thanks go to Professor Danuta Wróbel for valuable discussion and to Dr. Bolesław Barszcz for co-operation and giving me facilities for using his unpublished results of quantum chemical simulations.

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