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Photoexcited State Properties of H₂-Porphyrin/C₆₀-Based Rotaxanes as Studied by Time-Resolved EPR Spectroscopy

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Abstract

Light-driven intramolecular electron transfer (ET) and energy transfer (EnT) processes in two rotaxanes, the first containing two free base porphyrins and C₆₀ fullerene moieties incorporated around a Cu(I)bisphenanthroline core ((H₂P)₂-Cu(I)(phen)₂-C₆₀) and a second rotaxane lacking the fullerene moiety ((H₂P)₂-Cu(I)(phen)₂) were studied by X-band (9.5 GHz) time-resolved electron paramagnetic resonance (TREPR) spectroscopy. The experiments were performed in a frozen toluene and ethanol, and different phases of the nematic liquid crystal (E-7). It is demonstrated that the ET and EnT processes in the (H₂P)₂-Cu(I)(phen)₂-C₆₀ rotaxane in different media result in formation of the same charge separated state, namely (H₂P)₂^{•+}-Cu(I)(phen)₂^{•-}-C₆₀, while photoexcitation of the (H₂P)₂-Cu(I)(phen)₂ rotaxane does not induce noticeable transfer processes in these matrices. The results are discussed in terms of the high conformational mobility of the rotaxanes, which enables changes in the molecular topography and resultant modification of the rates and routes of photoinduced processes occurring in these systems. The parameters of the transfer processes are compared with those obtained in our previous study of (ZnP)₂-Cu(I)(phen)₂-C₆₀ and (ZnP)₂-Cu(I)(phen) rotaxanes under the same experimental conditions.

Keywords

Porphyrins; Fullerenes; Rotaxanes; Photoinduced Electron and Energy Transfer; Triplet State Time-Resolved EPR

Introduction

Rotaxanes are extraordinary supramolecular structures in which a macrocyclic ring is mechanically interlocked with a chain (thread) terminated by bulky stoppers to prevent dissociation.^{1,2} In such architectures, appended moieties are not chemically linked directly. Such structural organization results in high mobility of the rotaxane constituents as compared to that in "conventional" covalent arrays. In addition to the rotational and vibrational motions feasible in the chemically bonded ensembles, the rotaxane entities are able to perform translational movements relative to each other. Hence, these supramolecules could serve as building blocks for materials and devices whose properties and parameters can be varied by different external perturbations. In photoactive rotaxanes, such large amplitude conformational changes can be induced by light-driven electron transfer (ET) or/and energy transfer (EnT). The high mobility of the rotaxane components affects electronic

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coupling between appended donor and acceptor moieties, thus changing intramolecular ET and EnT routes and rates.^{3–9} In most cases, the rotaxane topology prevents close approach of the donor and acceptor entities, so that intramolecular electronic interactions between them must take place through a specially designed spacer. Thus, by choosing an appropriate spacer molecule, one can tune the forward and backward ET rates.¹⁰

In the rotaxanes and catenanes assembled by Sauvage's metal templating strategy, as in the present study, the key group is a bis-1,10-phenanthroline Cu(I) complex, Cu(I) (phen)_2^+ , with a PF_6^- counterion.¹¹ In addition, with advantages such as direct energy input and reversibility of ET processes that allow repetition of the operation at will, along with convenient time scale of the cycle, photoactive rotaxanes are particularly promising for various applications.¹² Here, we should underline the significant influence of the properties of the medium on both the conformational features of the rotaxane and the thermodynamic and kinetic parameters of ET and EnT processes in these supramolecules, which in turn, affects the efficiency of these processes.¹³ A detailed understanding of structure-function relationships in rotaxanes together with consideration of the solute-solvent interaction is required for the design and assembly of "smart" systems such as molecular machines and molecular motors,^{3,11,14,15} as well as model systems which faithfully mimic the processes occurring in the native photosynthetic apparatus.^{11,16}

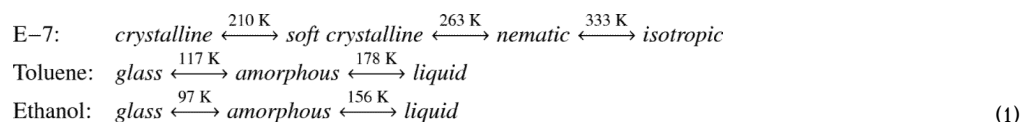
Recently we have demonstrated that the efficiencies and pathways of the light-driven ET and EnT processes in $(\text{ZnP})_2\text{-Cu(I)(phen)}_2$ and $(\text{ZnP})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ rotaxanes strongly depend upon the properties of their microenvironment, which is reflected by formation of distinct charge-separated states under different experimental conditions.¹³ More specifically, relaxation of the photoexcited entities in the rotaxanes occurs differently in glassy, amorphous, and liquid states of isotropic solvents as well as in the crystalline and nematic phases of liquid crystal (LC). We have attributed these findings to the high conformational mobility of the mechanically interlocked rotaxane systems, enabling conformational changes to take place depending on the microenvironment properties and the temperature, thus affecting ET and EnT efficiencies and routes. Here we extend our previous work on porphyrin/fullerene-based rotaxanes¹³ aiming to reveal the correlation between structure and function in these supramolecules. We report here on the light-driven processes in $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2$ (Figure 1a); and $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ (Figure 1b) rotaxanes, which differ from the previously studied supramolecules only by replacing Zn^{2+} by H_2 in the porphyrin core.

The experimental method employed in this study is X-band (9.5 GHz) time-resolved electron paramagnetic resonance (TREPR) combined with selective laser light excitation of the various moieties in the rotaxane. The measurements were performed in frozen toluene and in different phases of a nematic LC, E-7. High sensitivity, spectral- and time-resolution of the EPR spectroscopy, together with the use of magnetically oriented LC as a solvent, enable following of transient paramagnetic species in the system of interest in real time. Analysis of the TREPR spectra under different experimental conditions provides information not derivable from optical studies about dynamic, kinetic, and magnetic parameters associated with the ET precursors and intermediates. Thus, TREPR spectroscopy, which allows experiments over a wide range of solvents, temperatures, and time intervals, successfully complements optical spectroscopy in revealing the mechanisms associated with electron transfer (ET) processes.^{17,18}

Experimental

Toluene (A. C. S. Reagent, J. T. Baker Inc.) for sample preparation was dried over molecular sieves and kept under vacuum. Ethanol (Chromasolv, Absolute, HPLC grade,

Sigma-Aldrich) and LC (E-7, Merck Ltd.) were used without further purification. The phase transitions of the solvents are given below:



The rotaxanes used in the present study were prepared by treatment of the previously reported $(\text{ZnP})_2\text{-Cu(I)(phen)}_2^+$ and $(\text{ZnP})_2\text{-Cu(I)(phen)}_2^+\text{-C}_{60}$ compounds¹⁹ with trifluoroacetic acid. In a typical experiment, ZnP-rotaxane (0.021 mmol, 1 equiv) was dissolved in 5 mL of dichloromethane and 1 mL of trifluoroacetic acid was added to the purple solution. The green reaction mixture was stirred for 8 h in a well-closed vessel. The crude product was copiously washed with water (5×20 ml), dried over MgSO_4 filtered through paper and the solvent was removed under reduced pressure. The purple solid was redissolved in 5 ml of dichloromethane and a saturated solution of KPF_6 in methanol was added. The purple solution was stirred for 3 h to affect anion exchange. The solvents were removed under reduced pressure; the remaining insoluble purple solid was extracted with dichloromethane, filtered through paper and concentrated under reduced pressure. Final purification was achieved by column chromatography (SiO_2) using dichloromethane/methanol (98:2 v/v) as eluent.

$(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2^+$ rotaxane: Purple solid, 94% yield (0.064 g). ^1H NMR (CDCl_3), δ ppm: 8.99-8.79 (m, 16H), 8.42 (m, 4H), 8.29 (d, 4H), 8.23 (d, 4H), 8.03 (s, 12H), 8.01 (s, 2H), 7.97 (s, 2H), 7.79 (s, 6H), 7.66 (m, 4H), 7.21 (d, 4H), 7.16 (s, 2H), 7.02 (m, 4H), 6.38 (t, 1H), 6.02 (d, 4H), 5.68 (d, 4H), 4.6-3.5 (m, 35H), 1.47 (s, 108H), -2.81 (s, 2H). MALDI-TOF: m/z found 3228.88 $[\text{M} - \text{PF}_6]^+$, calculated 3228.61 for $\text{C}_{210}\text{H}_{220}\text{N}_{12}\text{O}_{16}\text{Cu}$.

$(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2^+\text{-C}_{60}$ rotaxane: Purple solid, 95% yield (0.077 g). ^1H NMR (CDCl_3), δ ppm: 8.99-8.79 (m, 16H), 8.45 (m, 4H), 8.27 (d, 4H), 8.20 (d, 4H), 8.06 (s, 12H), 8.03 (s, 2H), 7.99 (s, 2H), 7.77 (s, 6H), 7.68 (m, 4H), 7.22 (d, 4H), 7.03 (m, 4H), 6.01 (d, 4H), 5.68 (d, 4H), 4.6-3.5 (m, 32H), 1.47 (s, 108H), -2.85 (s, 2H). MALDI-TOF: m/z found 3882.98 $[\text{M} - \text{PF}_6]^+$, calculated 3882.56 for $\text{C}_{265}\text{H}_{214}\text{N}_{12}\text{O}_{16}\text{Cu}$.

The rotaxanes were first dissolved in toluene ($\sim 5 \times 10^{-4}$ M), which was then evaporated and the LC was introduced into the Pyrex tube. The samples were degassed by several freeze-pump-thaw cycles on a vacuum line and sealed under vacuum.

X-band TREPR experiments (response time of 150–200 ns) were performed in degassed 4 mm O.D. Pyrex tubes employing a Bruker ESP 380 EPR spectrometer with field modulation disconnected.²⁰ The EPR signals were taken from the microwave preamplifier and transferred to a Le Croy 9400 digital oscilloscope after being passed through a low-noise filter and amplified by a fast amplifier (10 dB). A frequency counter (EIP, Model 545) was used to monitor the microwave frequency. Estimation of the g-factors was performed employing magnetic field and microwave frequency controllers, namely a precision NMR Teslameter PT 2025 (Metrolab), and microwave frequency counter EIP 545, respectively. Transient traces of the EPR signals were acquired and accumulated on a PC through a GPIB interface. The spectra at different time windows after the laser pulse were reconstructed from the full set of data obtained over a chosen scan range of the magnetic field. The temperature was controlled by a Bruker variable-temperature unit (Model ER411 VT). The samples were illuminated by an OPO (Panther III, Continuum Corp.) pumped by the third harmonic (355 nm) of a Nd:Yag laser (Surelite II, Continuum Corp.): 7–10 mJ/pulse OPO output, 10 Hz repetition rate and 10 ns pulse duration).

The orientation of the LC director, L , with respect to the magnetic field, B , is determined by the sign of the anisotropy of the diamagnetic susceptibility, $\Delta\chi(\Delta\chi = \chi_{\parallel} - \chi_{\perp})$.²¹ Since $\Delta\chi$ is positive for E-7, the default orientation in the nematic phase is $L \parallel B$. Rotation of the frozen sample by 90° about an axis perpendicular to the external magnetic field yields the director orientation is $L \perp B$. Analysis of the TREPR line shapes was performed as described elsewhere.^{22,23} The radical pair (RP) spectra were analyzed in terms of spin correlated radical pair (SCRIP) and triplet radical pair (TRP) mechanisms.^{24–26}

In all EPR experiments, the spectra did not show any saturation effects over the wide microwave power range (15 – 93 mW) and the corresponding kinetics did not exhibit any oscillations, satisfying underdamping conditions.²⁷

The distances between the supramolecular entities were calculated employing HyperChem modeling, which allows computing the minimal energy molecular geometry in vacuum. Thus, in the condensed media the computed spacing of the rotaxane parts should be considered as estimates.

Results and Discussion

All TREPR experiments were performed employing selective excitation of the rotaxane constituents using laser light of suitable wavelengths, namely 460 and 532 nm. At 460 nm the absorption of the Cu(I)(phen)_2 moiety is maximal ($\kappa \approx 1700 \text{ cm}^{-1}\text{M}^{-1}$)²⁸ while the absorption of H_2P is relatively small ($\kappa \approx 4222 \text{ cm}^{-1}\text{M}^{-1}$),²⁹ At 532 nm, Cu(I)(phen)_2 absorption is low ($\kappa \approx 270 \text{ cm}^{-1}\text{M}^{-1}$), while H_2P absorption is high ($\kappa \approx 8910 \text{ cm}^{-1}\text{M}^{-1}$).²⁹ The extinction coefficients of C_{60} at 460 and 532 nm are $200 \text{ cm}^{-1}\text{M}^{-1}$ and $840 \text{ cm}^{-1}\text{M}^{-1}$, respectively.³⁰ Thus, the probabilities of light absorption by the $(\text{H}_2\text{P})_2$, Cu(I)(phen)_2 and C_{60} entities in the rotaxane correspond to the ratio of their extinction coefficients, namely 21:9:1 at 460 nm, and 33:1:3 at 532 nm. Therefore, upon 460 nm excitation of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2$, the probabilities to obtain the rotaxanes with photoexcited H_2P or Cu(phen)_2 entities should be initially comparable, while on excitation at 532 nm, the rotaxanes with photoexcited porphyrin entity should dominate. In the case of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$, H_2P and Cu(phen)_2 electronic excited states will both be generated upon irradiation at 460 nm, prevailing over electronically excited C_{60} , while most of the photons at 532 nm will be absorbed by H_2P (predominantly) and C_{60} (to a lesser extent) as compared to Cu(I)(phen)_2 .

The excited singlet and triplet states energies of the rotaxanes constituents are as follows: H_2TPP : 1.90 and 1.44 eV;³¹ Cu(I)(phen)_2 : 1.91 and 1.73 eV (averaged);^{32,33} and C_{60} : 1.80 and 1.57 eV, respectively.³⁴ The extinction coefficients (see above) and excited state energies for pristine 5,10,15,20-tetraphenylporphine H_2TPP are taken as being close to those of the porphyrin moiety in the rotaxanes studied. We also assume that the values of these parameters for all the moieties in the mechanically interlocked supramolecular systems are similar to those of the corresponding pristine compounds.

It is worth noting that all of the above parameters were determined in liquid isotropic solvents and may slightly change under our experimental conditions, so they were used only as estimates. Unfortunately, the corresponding precise values in the frozen isotropic solvents and LC matrices are not available.

Since the quenching routes of the photoexcited states of the chromophores depend on their microenvironment,³⁵ TREPR experiments were performed in isotropic non-polar (toluene, dielectric constant $\epsilon = 2.38$)³⁶ and polar (ethanol, $\epsilon = 25.3$)³⁶ solvents as well as in the anisotropic LC E-7 ($\epsilon_{\parallel} = 19.0$, $\epsilon_{\perp} = 6.2$)³⁷ matrices over a wide range of temperatures, corresponding to the different states/phases of the rotaxane microenvironment.

(H₂P)₂-Cu(I)(phen)₂

Isotropic solvent—This rotaxane upon photoexcitation at 460 or 532 nm in frozen toluene and ethanol exhibits practically identical polarized triplet spectra with absorption/emission (a/e) electron spin polarization (ESP) patterns and a spectral width of ~70 mT. Figure 2 presents the TREPR spectrum of (H₂P)₂-Cu(I)(phen)₂ in toluene at 140 K following 460 nm photoexcitation. The spectrum of the rotaxane in frozen ethanol is nearly the same (not shown).

Computer simulations of the spectra provided us with zero-field splitting (ZFS) parameters |D| and |E| of the paramagnetic species as well as relative population ratios of their triplet sublevels. These are very close to the corresponding ones found earlier for H₂TPP under the same experimental conditions (Table 1).^{22,38} This finding allowed us to assign the observed broad spectra to the lowest triplet state of H₂P. No evidence was obtained for formation of charge-separated states under these conditions (see below).

Liquid crystal—Photoexcitation of (H₂P)₂-Cu(I)(phen)₂ at 460 nm in the crystalline phase of E-7 (170 K) gives rise to the spectra depicted in Figure 3. At both L || B and L ⊥ B orientations, the spectra consist of a broad signal with g-value of 2.00 and e,a polarization pattern, which does not change in time.

The data from computer simulations of the spectra are presented in Table 1 together with the corresponding parameters for the pristine porphyrin (H₂TPP) taken under the same experimental conditions.^{22,38} The close similarities of these parameters show that the observed broad spectra can be ascribed to the lowest triplet excited state of the porphyrin entity in (H₂P)₂-Cu(I)(phen)₂.

Photoexcitation of (H₂P)₂-Cu(I)(phen)₂ in the crystalline phase at 532 nm at L || B and L ⊥ B orientations results only in the broad spectra that are essentially identical to those observed upon 460 nm excitation.

The spectra of (H₂P)₂-Cu(I)(phen)₂ in the soft crystalline (240 K) and the nematic phases (300 K) of the LC obtained at both 460 and 532 nm excitation exhibit the spectral lineshape and magnetic parameters that are typical for pristine H₂TPP triplet under the corresponding experimental conditions (Table 1). As in the case of the isotropic solvents, all TREPR spectra detected in LC over a wide range of temperatures are characterized by high signal-to-noise ratio.

These findings allow us to exclude the occurrence of substantial EnT from the Cu(I)(phen)₂ triplet state to the triplet of H₂P, because such triplet-triplet EnT should cause distortion of the observed spectral lineshape as compared to the pristine compound, which is not the case.^{39,40} Nevertheless, the slight splitting detected in the L || B signal (Figure 3) indicates that this EnT process might be occurring to a small extent. Furthermore, no evidence for ET (i.e., charge-separated state formation) was observed in the experiments with the (H₂P)₂-Cu(I)(phen)₂ rotaxane. The lack of observable intramolecular ET and EnT between the moieties in (H₂P)₂-Cu(I)(phen)₂ is in contrast to the findings in the recently studied (ZnP)₂-Cu(I)(phen)₂ rotaxane,¹¹ and can be rationalized as follows. According to HyperChem molecular modeling (Figure 4), the distance between the core centers of the porphyrin and copper phenanthroline moieties in (H₂P)₂-Cu(I)(phen)₂ is noticeably larger in (H₂P)₂-Cu(I)(phen)₂ than in (ZnP)₂-Cu(I)(phen)₂,¹³ namely 22 Å vs 18 Å. This difference is very significant in terms of the strong non-linear dependence of the ET and EnT efficiencies on the distance between electron donor and acceptor moieties.⁴¹ Moreover, the oxidation potential for H₂P is nearly twice as large as that for ZnP (0.56 V vs 0.3 V, as measured with respect to ferrocene-ferrocenium).⁴² Even considering the various (H₂P)₂-Cu(I)(phen)₂

rotaxane conformations that can be realized in toluene, ethanol and LC media at different temperatures, the result of the combination of these factors is that photoinduced ET and EnT processes are not sufficiently efficient to be detectable in this rotaxane under our experimental conditions.

(H₂P)₂-Cu(I)(phen)₂-C₆₀

Isotropic solvents—Figure 5 shows the TREPR spectrum of the rotaxane (H₂P)₂-Cu(I)(phen)₂-C₆₀ after excitation at 532 nm in frozen toluene (140 K). Inspection of the figure shows that the spectrum is composed of two signals, namely a broad signal of 78 mT width and polarization pattern e,e/a,a and superimposed on it a sharp e/a signal with peak-to-peak width $\Delta H_{pp} \sim 0.8$ mT. Both these signals possess g-values of 2.00 and do not change their phase in time. Analysis of the broad signal shows that it is essentially identical to the TREPR signal obtained from H₂TPP under the same experimental conditions, and can be assigned to the lowest triplet state of the H₂P moiety. As to the narrow signal, we cannot attribute it to the photoexcited states of either Cu(I)(phen)₂ or C₆₀ entities at both excitation wavelengths. As to the former, it was established for the similar rotaxanes¹⁹ that photoexcitation of Cu(I)(phen)₂ results in the formation of the metal-to-ligand charge transfer state (MLCT), which possess too short lifetime (~ 5 ns) in isotropic solvents to be detected in our experimental setup. The TREPR spectrum of C₆₀ in frozen toluene displays opposite (a/e) polarization pattern and a linewidth ΔH_{pp} which is more than 10 times greater than that of our narrow signal.^{43,44} Therefore, we assign the narrow TREPR signal to a charge-separated state formed in (H₂P)₂-Cu(I)(phen)₂-C₆₀.

Photoexcitation of the sample at 460 nm gives rise, in addition to the H₂P and RP spectra, to an a/e signal of 6.4 mT width, which was assigned to the lowest triplet state of C₆₀. It should be noted that under our experimental conditions with impeded diffusion, i. e., in frozen and viscous matrices, two pathways leading to a charge-separated state can account for the observed multiplet radical pair (RP) signal, i. e., triplet radical pair (TRP) and weakly coupled spin-correlated radical pair (SCRPP) mechanisms. Well elaborated theory of these mechanisms relying on the RP spectrum analysis, allows one to draw conclusions about the precursor and mechanism of RP formation and identify its participants. For example, the linewidth of the RP signal is governed by exchange and dipolar interactions. Based on the linewidth of the narrow signal we can exclude the possibility that the origin of the observed narrow signal in (H₂P)₂-Cu(I)(phen)₂-C₆₀ is a charge-separated state such as (H₂P)₂^{•+}-Cu(I)(phen)₂-C₆₀^{•-} or (H₂P)₂^{•-}-Cu(I)(phen)₂-C₆₀^{•+}. This is because the H₂P and C₆₀ in the former rotaxane are still far apart, despite the lowest energy "folded" conformation of (H₂P)₂-Cu(I)(phen)₂-C₆₀ (see Figure 6) as compared to the "stretched" conformation of (H₂P)₂-Cu(I)(phen)₂ (Figure 4). This conformational effect was previously proposed for analogous ZnP-C₆₀ rotaxanes, and is attributed to attractive interactions between porphyrin and C₆₀ moieties.⁴⁵ At the distance of 26 Å between the centers of the fullerene and nearest porphyrin in (H₂P)₂-Cu(I)(phen)₂-C₆₀, the exchange interaction is negligibly small, and the width of the signal should be governed only by dipolar interactions. In turn, the point dipole approximation,

$$|D| = 3/4[(g\beta)^2/r^3] \quad (2)$$

with a g-factor of 2.00, β as the Bohr magneton, and $r \sim 26$ Å, gives a value of 0.16 mT for the RP parameter ΔH_{pp} ($\Delta H_{pp} \sim D$), which is 5 times less than the signal presented in Figure 5 (the RP formed by ET from the far H₂P to C₆₀, with a center-to-center distance of ~ 36 Å, should display a much smaller ΔH_{pp} value of ~ 0.06 mT). Thus, we suggest that the observed narrow signal is a result of ET either between H₂P and Cu(I)(phen)₂ or between Cu(I)(phen)₂ and C₆₀. Both these suggestions will be discussed below. Since this rotaxane

does not dissolve in ethanol, we could not carry out corresponding experiments in this polar solvent for comparison.

Liquid crystal—It is well established that analysis of the RP signal phase behavior in magnetically oriented LC, namely at $L \parallel B$ and $L \perp B$ orientations of the sample in a crystalline phase of LC, allows one to draw conclusions on the nature of this species, namely to discern a TRP or an SCRP mechanism.^{17,18} This, in turn, significantly facilitates identification of the RP constituents, particularly in multicomponent systems.^{20,46,47} TREPR experiments were performed in the nematic (room temperature), soft crystalline (240 K), and crystalline (170 K) phases of the LC using both 460 and 532 nm photoexcitation. Figure 7 presents the time evolution of the $(H_2P)_2-Cu(I)(phen)_2-C_{60}$ triplet spectra obtained in the soft crystalline phase (240K) of LC after 532 nm excitation. Analysis of the spectra shows that the broad signal is practically identical to the triplet spectrum of H_2TTP observed under the same experimental conditions and can be assigned to the lowest H_2P triplet state.^{22,38} As to the superimposed narrow signal, its g -value, linewidth, and polarization pattern coincide with those found for the RP signal observed from photoexcited $H_2P-Cu(I)(phen)_2-C_{60}$ in frozen toluene (Figure 5). Furthermore, examination of the spectral time evolution shows that decay of this signal to the point of disappearance occurs without any change in the polarization pattern seen in Figure 7. This finding indicates that the precursor of the charge-separated state accounting for the narrow signal remains unchanged with time.^{20,46,47}

Photoexcitation of the rotaxane in the crystalline phase of the LC gives rise to the spectra presented in Figure 8. These spectra are composed of a broad signal, a significantly narrower signal, and a narrow line. According to its parameters, the broad signal is again assigned to the lowest triplet states of H_2P (see above), while the narrower spectrum is attributed to the lowest energy C_{60} triplet state^{43,44} as all its parameters are in a good agreement with those observed in the triplet spectra of pristine C_{60} under the same experimental conditions.^{43,44} The narrowest signal in Figure 8 is again attributed to the RP, which was formed as a result of photoinduced charge separation.

The polarization patterns of all these signals are the same at both $L \parallel B$ and $L \perp B$ orientations and do not change with time. The finding that the phase of the RP signal does not depend on the orientation of the sample relative to the external magnetic field points to the mechanism of RP formation. More specifically, for weakly coupled SCRP with small values of ZFS parameter D and exchange interaction J , the phase of the signal should depend on the molecular orientation of the RP with respect to the magnetic field^{25,48}

$$D_{zz}=D(3 \cos^2 \xi - 1) \quad (3)$$

where D is the dipolar interaction and ξ is the angle between the RP dipolar axis and the magnetic field direction. Taking into account that $J \rightarrow 0$ in a weakly coupled SCRP, one can conclude that in such pairs the dominant interaction between the constituents is angle dependent dipolar coupling.²⁵ Thus, the phase inversion of the RP spectrum upon sample rotation in the solid phase of the LC is evident from eq 2 when the dipolar angle ξ is replaced by $(\xi + 90^\circ)$.^{46,49} Rotation of the sample by 90° should result in inversion of the RP signal (from e/a to a/e), in contrast to the observed signal phase behavior. On the other hand, for a strongly coupled TRP the RP phase should remain unchanged at $L \parallel B$ and $L \perp B$ orientations, which is the case.²⁵ Therefore, we assign the observed narrow signal to the TRP, which is formed as a result of photoexcited ET in $H_2P-Cu(I)(phen)_2-C_{60}$ rotaxane.

Since the centers of the donor and acceptor moieties in both possible pairs $H_2P-Cu(I)(phen)_2$ and $Cu(I)(phen)_2-C_{60}$ are separated by almost the same distance (~ 13 Å), as seen in Figure

6, the RP linewidth alone can not serve as evidence for identification of the observed RP. This is because in both these pairs dipolar and exchange interactions should contribute similarly to the signal width. Thus, for establishing the RP participants in toluene and in LC we will take into account that the TRP signal should be centered about the mean value of the g -factors of the RP constituents. In this context, we will now analyze all possible charge-separated states in this rotaxane both in toluene and in LC matrices:

(a) $\text{H}_2\text{P}^{\bullet+}\text{-Cu(I)(phen)}_2^{\bullet-}$. The g -values of $\text{H}_2\text{TPP}^{\bullet+}$ and $\text{Cu(I)(phen)}_2^{\bullet-}$ are 2.0004⁵⁰ and 2.0023, respectively. Thus, g -value of the RP composed of these constituents should be equal to their mean value, namely 2.0014, which is the case; (b) $\text{Cu(II)(phen)}_2\text{-C}_{60}^{\bullet-}$. In this case RP signal should be centered around a g -value of 2.0650, which is the average of the corresponding values for Cu(II)(phen)_2 ($g_{\text{iso}} \sim 2.13$)⁵¹ and $\text{C}_{60}^{\bullet-}$ ($g \sim 1.9999$)⁵² which is inconsistent with the experimental data; (c) $\text{Cu(II)(phen)}_2\text{-H}_2\text{P}^{\bullet-}$. This RP should possess a g -factor of 2.0664, (mean value of $g_{\text{iso}} \sim 2.13$ for Cu(II)(phen)_2 ⁵¹ and 2.0027 for $\text{H}_2\text{TPP}^{\bullet-}$ ⁵³), which again is not in accord with the experimental data; (d) $\text{C}_{60}^{\bullet+}\text{-Cu(0)(phen)}_2$. For this charge separation, calculation of the free energy change was performed employing the expression taking into account the Coulombic interaction between the RP participants as well as the ion solvation energy, i.e., the corrections required in the case when the solvents for the ET and electrochemical measurements are different:^{31,35,54,55}

$$\Delta G^0 = E_{\text{ox}} - E_{\text{red}} - 14.32(1/\epsilon_s R_D^{\bullet+} A^{\bullet-}) + 14.32(1/2R_D + 1/2R_A)(1/\epsilon_s + 1/\epsilon_p) \quad (4)$$

where E_{ox} and E_{red} are oxidation and reduction potentials of the donor and acceptor, respectively; ϵ_s is the dielectric constant of the solvent; $R_D^{\bullet+} A^{\bullet-}$, R_D , and R_A are the distance between the participants in the RP and radii of the donor and acceptor (all in Å), respectively; ϵ_p is the average value of the dielectric constants of the solvents where the redox potentials of the donor and acceptor were measured, namely 1,1,2,2-tetrachlorethane ($\epsilon = 8.42$) and acetonitrile ($\epsilon = 37.5$). Here, we have used the following data: the one-electron oxidation potential of C_{60} donor: $E_{\text{ox}} \sim 1.26$ V,⁵⁶ and one-electron reduction potential of Cu(I)(phen)_2 acceptor: $E_{\text{red}} \sim -2.18$ V,⁵⁷ (both potentials were measured vs ferrocene); $R_D^{\bullet+} A^{\bullet-} \approx 13$ Å (from HyperChem); $R_D \approx 5$ Å,²⁸ and $R_A \approx 4$ Å;⁵⁸ $\epsilon_p \approx 23$; the dielectric constant of toluene at 140 K was calculated as 2.78;⁵⁹ the dielectric constant of LC (10.5) was calculated⁶⁰ as the average of the corresponding perpendicular and parallel values taken at room temperature (unfortunately, the temperature dependence of dielectric constant of the LC is not available). The calculated free energy change for electron transfer from C_{60} to the Cu(I) complex indicate values of 4 eV in toluene and 3.5 eV in the LC show that under the present experimental conditions (the photon energies of the 460 and 532 nm light are ~ 2.7 eV and ~ 2.3 eV, respectively) this process can be ruled out on thermodynamic grounds.

Thus, we conclude that the RP observed in our experiments with $\text{H}_2\text{P-Cu(I)(phen)}_2\text{-C}_{60}$ rotaxane is $\text{H}_2\text{P}^{\bullet+}\text{-Cu(I)(phen)}_2^{\bullet-}$. We propose the following scheme for the RP formation. After a direct or nondirect (via EnT from photoexcited H_2P) excitation of the Cu(I)(phen)_2 the MLCT state, i.e., $\text{Cu(II)(phen)}_2^{\bullet-}$ is formed, where the electron is mostly localized on a phen ligand.^{28,61} Cu(II) ion in this MLCT is a very powerful oxidant, which oxidizes the H_2P entity, similarly to the reaction found in related MLCT systems.⁶² As a result of this process, the $\text{H}_2\text{P}^{\bullet+}\text{-Cu(I)(phen)}_2^{\bullet-}$ RP is generated and accounts for the observed narrow signal. Our proposed scheme is depicted in Figure 9.

As was stated above, the linewidth of the TRP is governed by dipolar and exchange interactions, both of which are operative at a distance of 13 Å between the RP constituents and contribute to the observed RP signal width $\Delta H_{\text{pp}} \sim 0.8$ mT. Since the transferred

electron in the MLCT state is mostly localized on one of the ligands,⁶¹ the presented value of 13 Å is the average distance between the center of the H₂P ring and the Cu ion. The point dipole approximation (eq 1) gives ZFS parameter $|D|$ for the RP as ~ 1.3 mT. The EPR spectral linewidth of H₂P^{•+} is $\Delta H_{pp} \sim 0.3$ mT,⁵⁰ and one can suppose that the EPR linewidth of the phenanthroline radical should be typical of organic radicals, i.e., on the order of units of mT. Since the D parameter of the RP is usually negative, one can assume that for the observed RP width, namely $\Delta H_{pp} \sim 0.8$ mT, the J value is several mT and possesses a positive sign, which is reasonable at such distances.^{63–65} Taking into account these estimates as well as the polarization pattern e/a of the RP signal, we suggest that the precursor of the implicated charge-separated state is a singlet state.^{25,66,67}

This implies that after rapid charge separation, the electron spins in the RP are initially in a singlet configuration. Then, fast singlet-triplet mixing occurs resulting in the formation of a relatively long-lived triplet spin configuration of the RP, which is detected in the experiments.^{25,66,67}

(H₂P)₂-Cu(I)(phen)₂ vs (ZnP)₂-Cu(I)(phen)₂

Comparison of the presented results with those obtained previously¹³ reveals significant differences in the photoinduced processes occurring in the H₂P- and ZnP-stoppered rotaxanes. Both of these rotaxanes in the frozen isotropic solvents, i.e., toluene and ethanol, at both photoexcitation wavelengths exhibit only spectra corresponding to the triplet states of the porphyrin moieties. However in LC media the behavior of the rotaxanes becomes different. In all phases of the LC at both 460 and 532 nm the (H₂P)₂-Cu(I)(phen)₂ rotaxane shows only the triplet spectra of the H₂P, with no evidence of any charge-separated state. On the other hand, the (ZnP)₂-Cu(I)(phen)₂ displays the same behavior only when excited at 532 nm, i.e., only the triplet state of the ZnP moiety is observed in all LC phases. In contrast, at 460 nm excitation, this rotaxane also exhibits, in addition to the ZnP triplet spectrum, the signal of the charge separated state (ZnP)₂^{•+}-Cu(I)(phen)₂^{•-}, which was detected in the crystalline, soft crystalline and nematic phases of the LC. This observation can be explained by the low quantum yield for MLCT formation directly using 532 nm photoexcitation, due to the low light absorption of Cu(I)(phen)₂, as well as indirectly by inefficient EnT from the electronically excited ZnP to Cu(I)(phen)₂. As noted above, generation of the MLCT state is required for oxidizing the ZnP. The absence of noticeable ET on excitation of (H₂P)₂-Cu(I)(phen)₂ as compared to (ZnP)₂-Cu(I)(phen)₂ can be ascribed to the longer donor-acceptor separation in the former rotaxane and significantly higher oxidation potential of the H₂P relatively to that of the ZnP, as discussed earlier.

(H₂P)₂-Cu(I)(phen)₂-C₆₀ vs (ZnP)₂-Cu(I)(phen)₂-C₆₀

In a frozen toluene matrix (140 K) at both excitation wavelengths, TREPR spectra of (H₂P)₂-Cu(I)(phen)₂-C₆₀ exhibit signals for the H₂P and C₆₀ triplet states as well as the RP signal. (This compound does not dissolve in ethanol). The RP signal is assigned to the charge separated state (H₂P)₂^{•+}-Cu(I)(phen)₂^{•-}. As for the spectra of the (ZnP)₂-Cu(I)(phen)₂-C₆₀ in frozen toluene (140 K), they also correspond to the ZnP and C₆₀ triplets, as well as RP. However, the RP in this case was associated with a different charge-separated state, namely Cu(I)(phen)₂^{•+}-C₆₀^{•-}, which was formed by a different ET pathway.¹¹

Photoexcited (H₂P)₂-Cu(I)(phen)₂-C₆₀ in the crystalline and soft crystalline phases of LC gives rise to triplet signals of H₂P, C₆₀, and a RP state at both 460 and 532 nm excitations. In the nematic phase of LC the spectra of these species were detected only at 460 nm, while irradiation at 532 nm results in the H₂P triplet spectra only. We propose, for the reasons cited earlier, that the charge-separated state (H₂P)₂^{•+}-Cu(I)(phen)₂^{•-} accounts for the RP signal. The previously studied (ZnP)₂-Cu(I)(phen)₂-C₆₀ rotaxane under photoexcitation by

460 nm exhibits triplet signals for ZnP, C₆₀, and the RP state (ZnP)₂^{•+}-Cu(I)(phen)₂^{•-} in all phases of the LC. When excited at 532 nm, only the triplet signals of the ZnP and C₆₀ are detected. It is noteworthy that in the LC medium both charge-separated states are formed in this system as a result of ET between the porphyrin and copper phenanthroline moieties.

Comparison of the extinction coefficients of the (H₂P)₂-Cu(I)(phen)₂-C₆₀ components together with the inspection of the corresponding triplet spectra leads to the following conclusion regarding the efficiency of photoinduced EnT between the rotaxane constituents. In all solvents at all experimental conditions the intensity of the fullerene triplet spectrum is significantly higher at 460 nm than at 532 nm. This finding indicates that the efficiency of EnT from Cu(I)(phen)₂ to C₆₀ is much higher under direct excitation of the Cu(I)(phen)₂ moiety (at 460 nm) as compared to that under its non-direct excitation at 532 nm following EnT from photoexcited H₂P.

The "stretched" (H₂P)₂-Cu(I)(phen)₂ and "folded" (H₂P)₂-Cu(I)(phen)₂-C₆₀ rotaxanes in this study demonstrate the influence of the high conformational mobility of the rotaxanes on the light-driven processes occurring in these mechanically interlocked supramolecules. Certainly, attachment of C₆₀ to the (H₂P)₂-Cu(I)(phen)₂ rotaxane, where the porphyrin parts are separated from the fullerene by ~22 Å (Figure 6), causes drastic conformational changes in the resultant (H₂P)₂-Cu(I)(phen)₂-C₆₀ rotaxane, where one of the porphyrins approaches the Cu(I)(phen)₂ by ~13 Å. We believe that this is the reason why photoinduced ET between the H₂P and Cu(I)(phen)₂ moieties becomes substantially operative only in the "folded" rotaxane structure.

Conclusions

Analysis of the structure-function relationships in the free base porphyrin rotaxanes and the previously studied ZnP analogous systems¹³ is in line with our suggestion that the changes in rotaxane conformation combined with the variation in the solvent properties strongly affects the thermodynamic parameters of the relevant ET reactions, which in turn significantly modifies the rates and routes of the ET and EnT processes occurring upon electronic excitation. In this regard, it would be of interest to compare the behavior of the conformationally flexible rotaxanes with that of more rigid analogous catenanes.

Hence, establishing a structure-medium-function correlation in mechanically-interlocked supramolecules such as those discussed here may serve as a basis for fine tuning of light-driven

Acknowledgments

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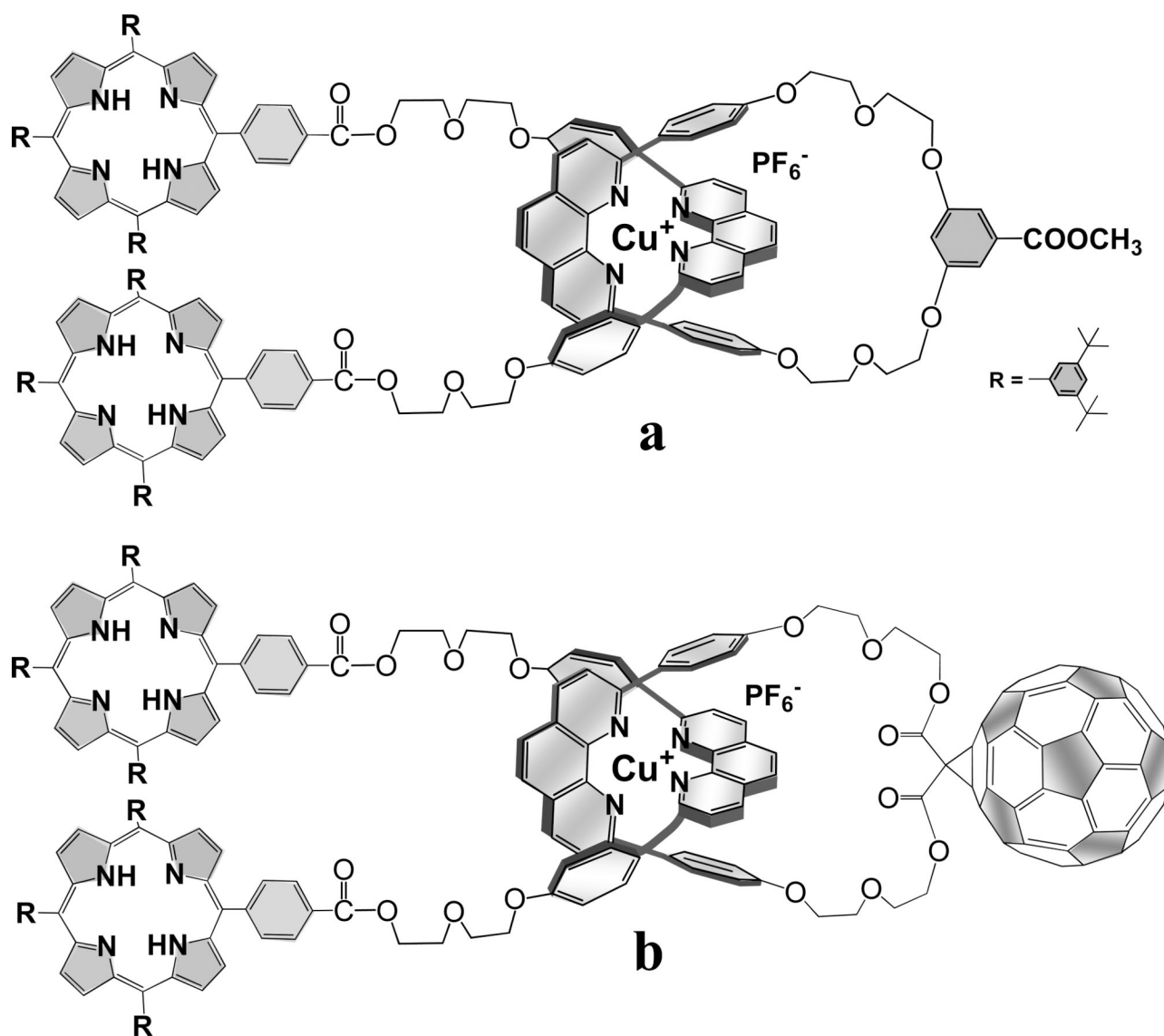


Figure 1.
The structures of **a**: $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2$ and **b**: $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ rotaxanes.

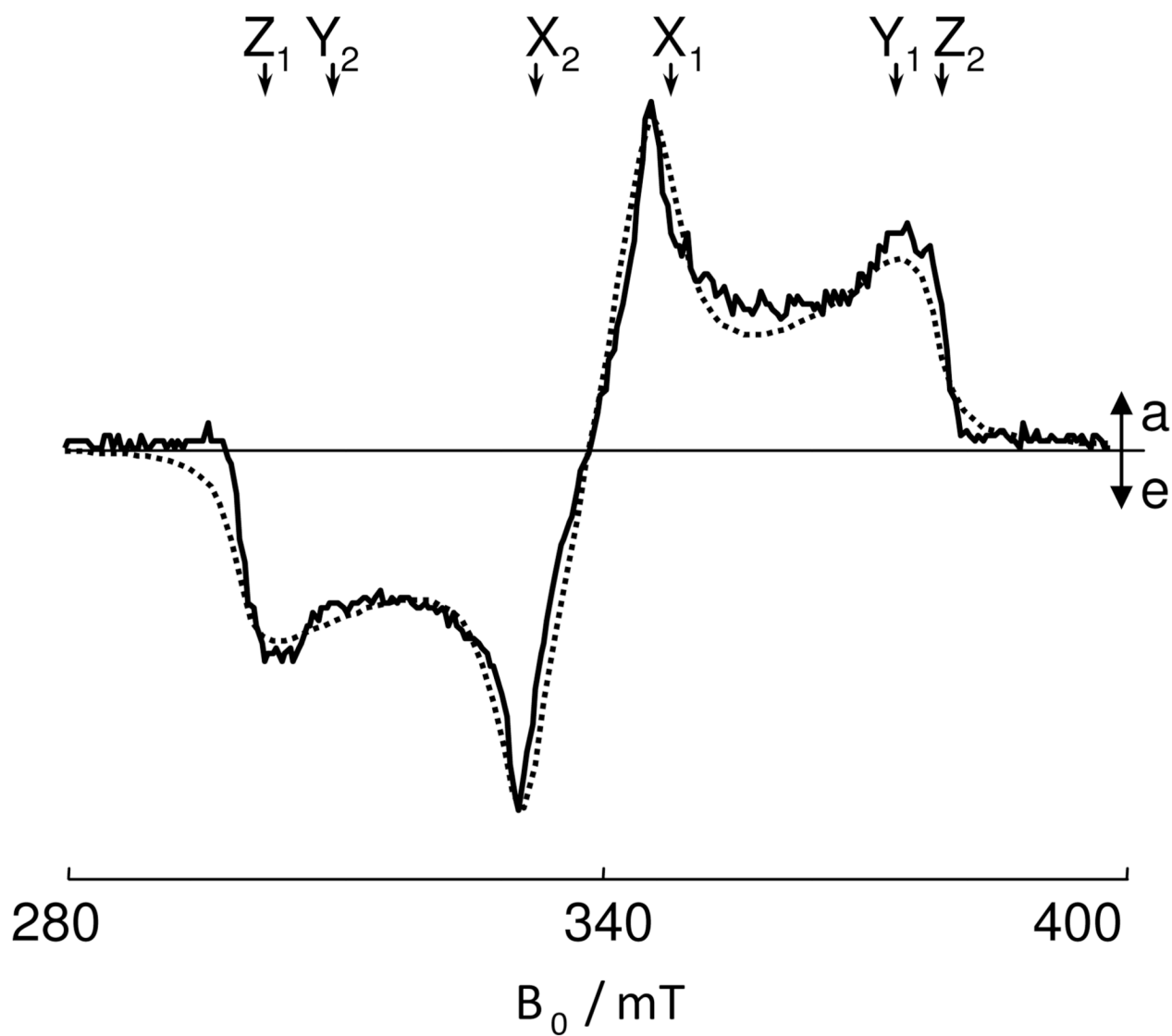


Figure 2.
TREPR spectrum of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2$ in frozen toluene (140 K) at 460 nm excitation, 1300 ns after the laser pulse.

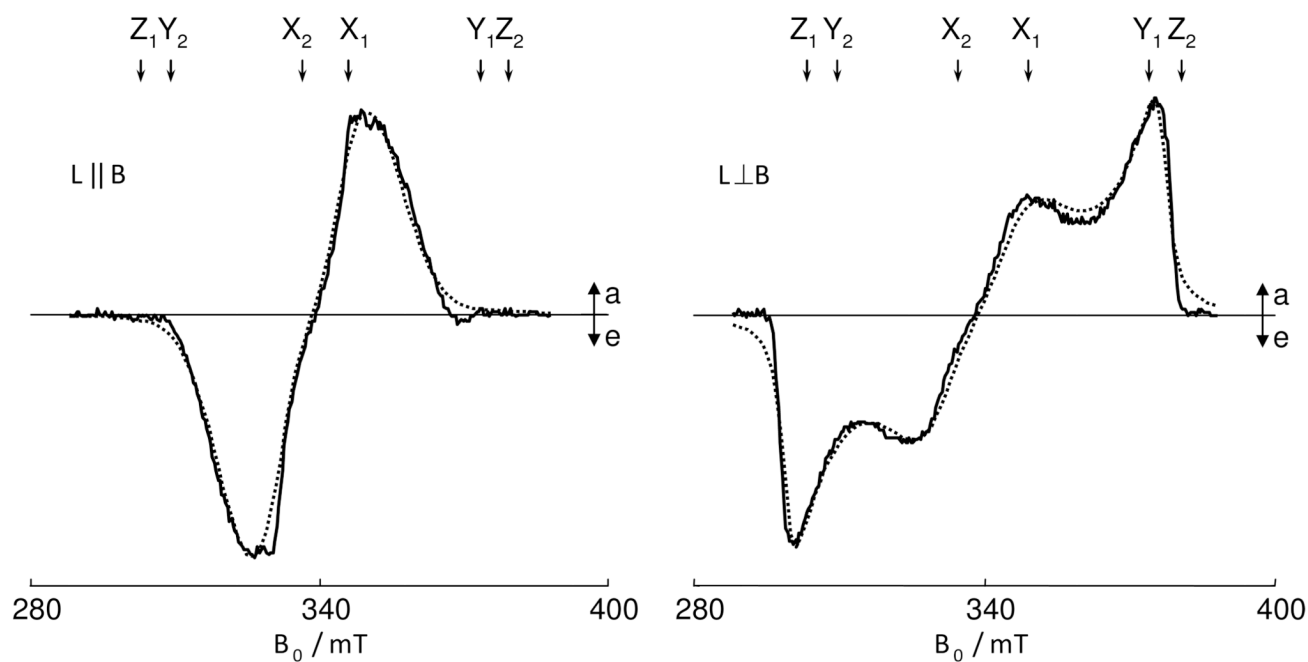


Figure 3.
TREPR spectra of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2$ in LC, 170 K photoexcitation at 460nm, 1150 ns after the laser pulse.

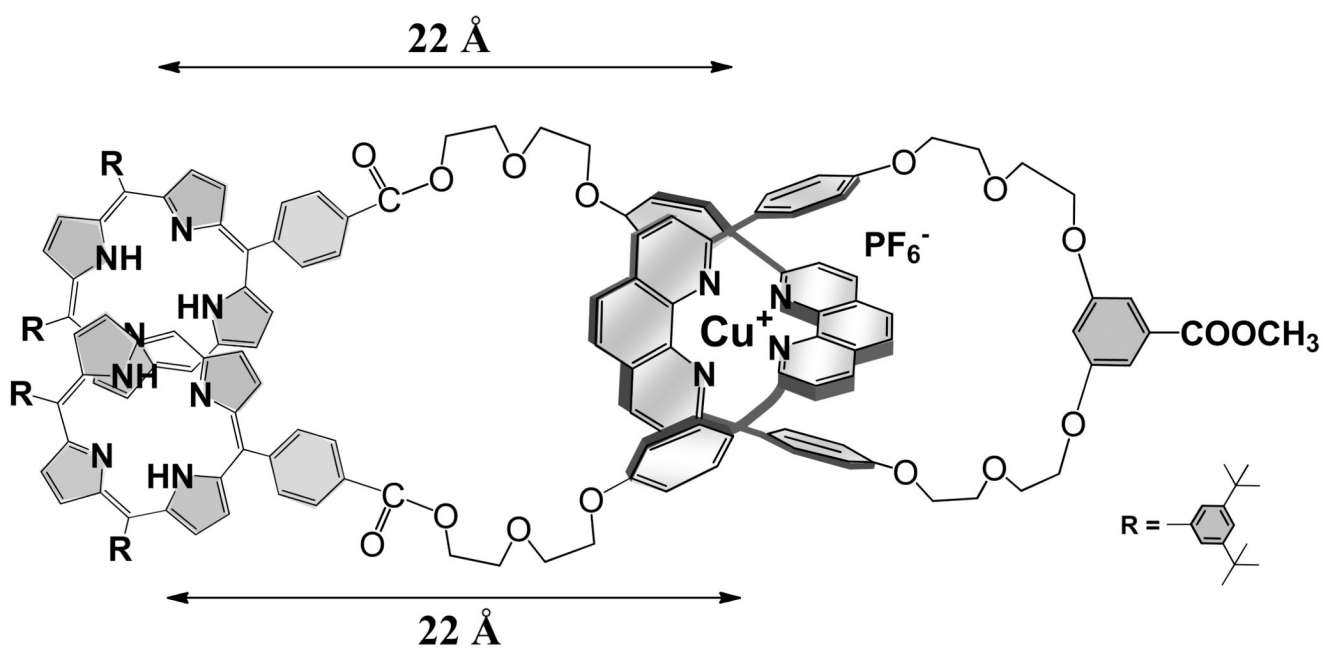


Figure 4.
HyperChem structure of (H₂P)₂-Cu(I)(phen)₂.

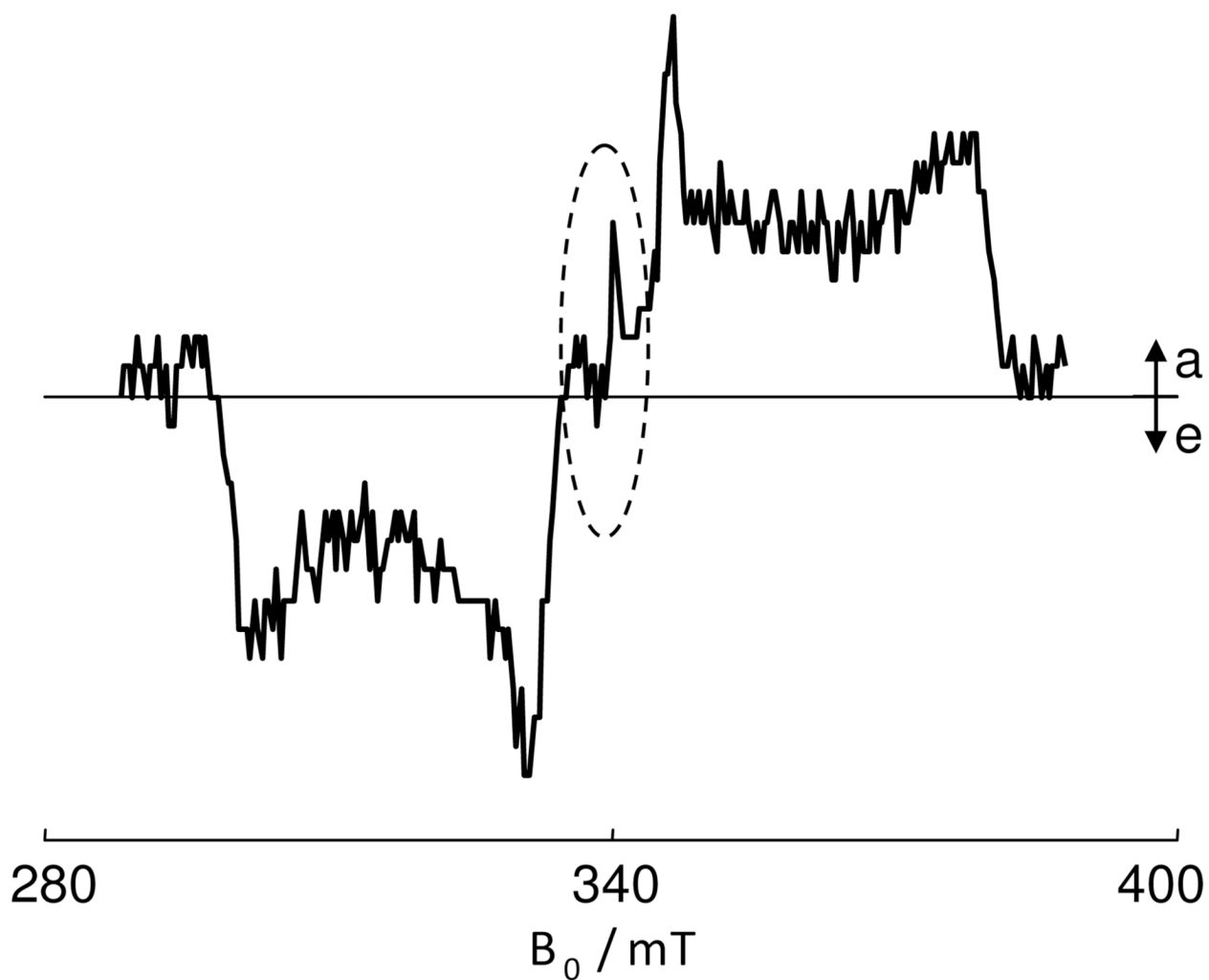


Figure 5.
TREPR spectrum of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ in frozen toluene (140 K) at 532 nm excitation, 700 ns after the laser pulse.

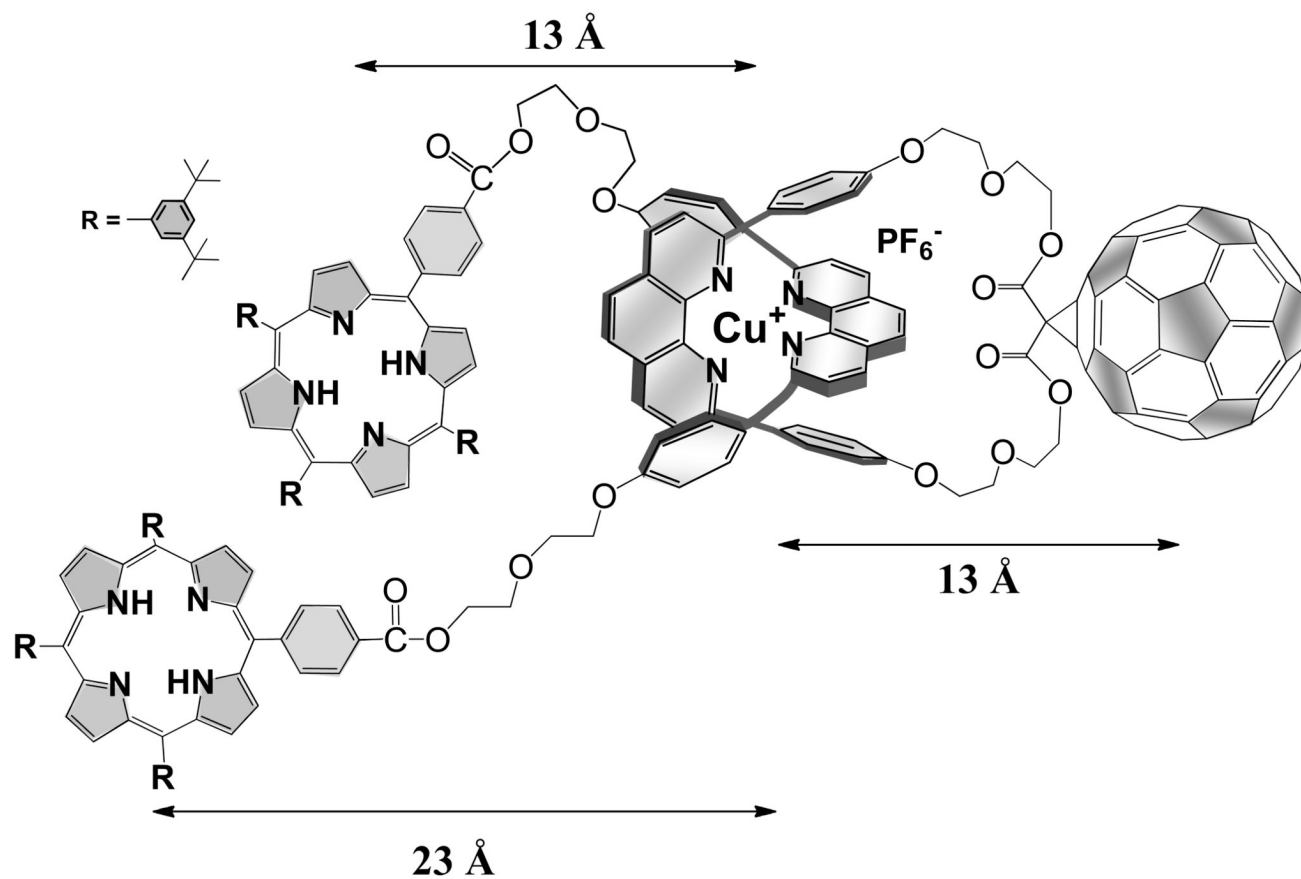


Figure 6.
HyperChem structure of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$.

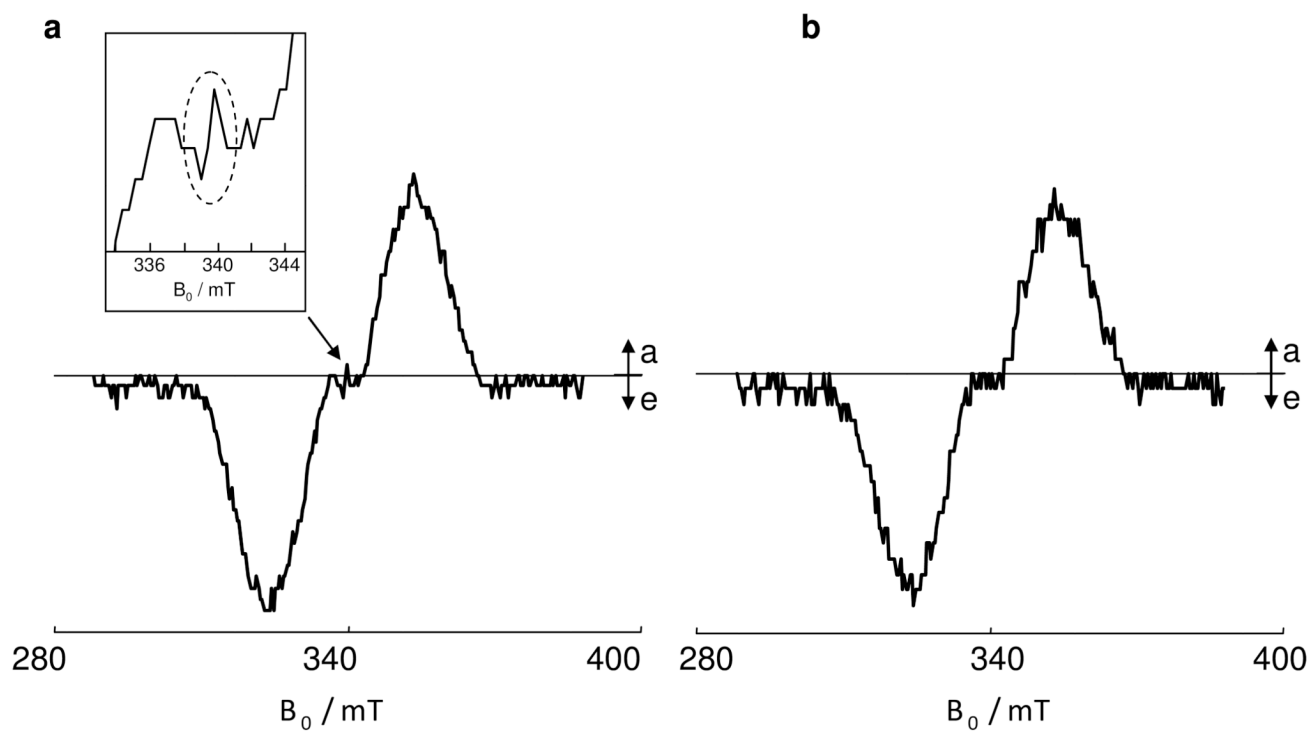


Figure 7. TREPR spectrum of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ in soft crystalline phase of LC (240 K) at 532 nm excitation, a: 1100 ns b: 2620 ns after the laser pulse. Inset: enlarged narrow signal.

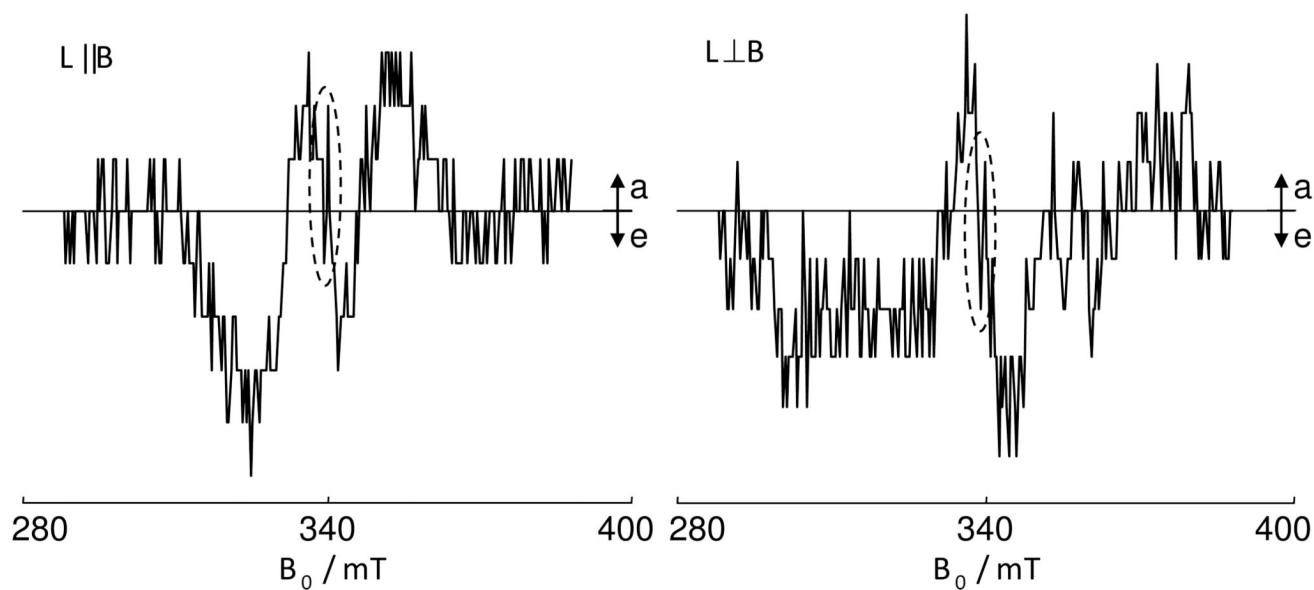


Figure 8.

TREPR spectra of $(\text{H}_2\text{P})_2\text{-Cu(I)(phen)}_2\text{-C}_{60}$ in LC at 170 K at $L||B$ and $L \perp B$ orientations. The spectra were observed using photoexcitation at 460nm in a time window of 780–900 ns, where the RP signal is maximal.

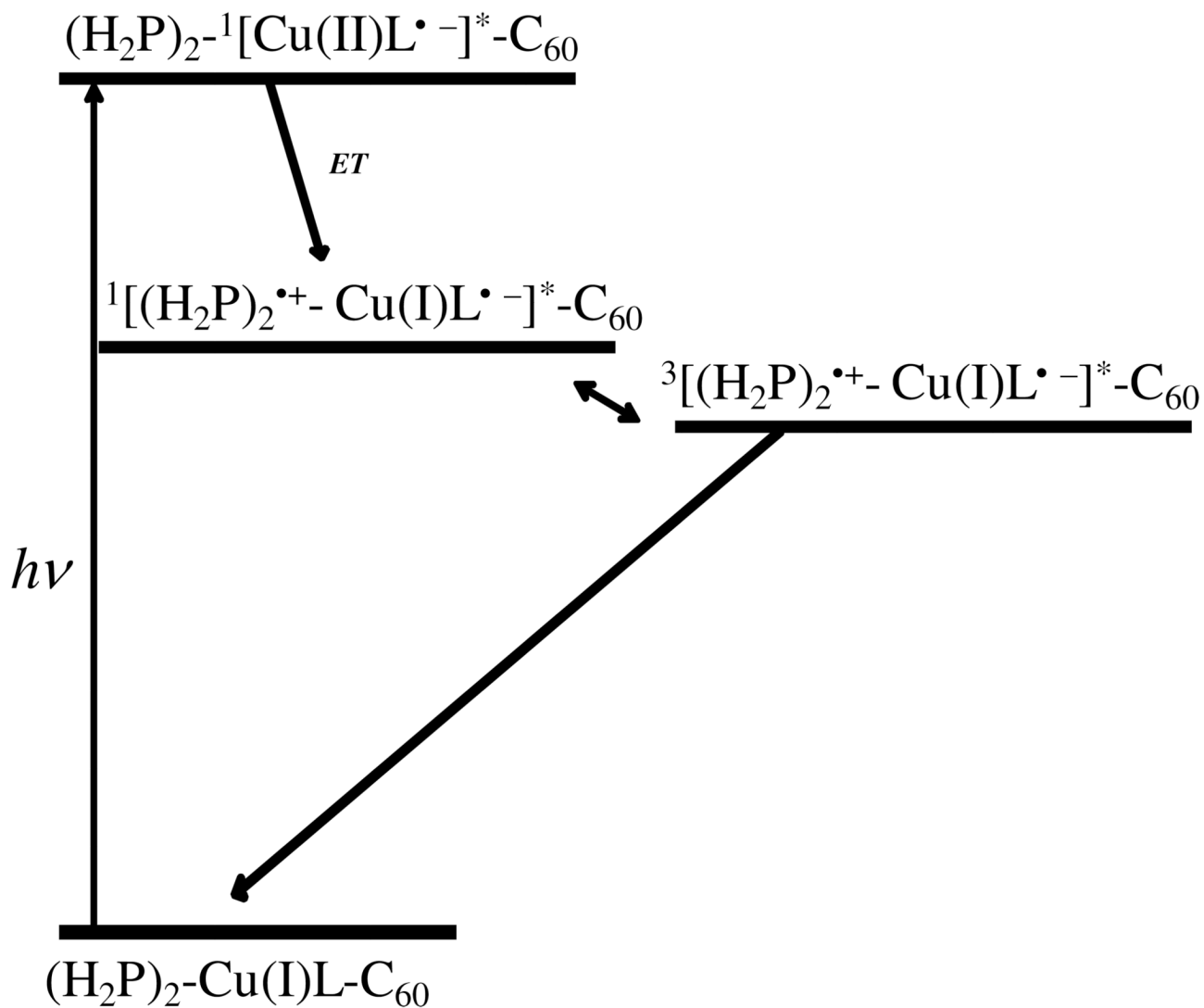


Figure 9.
General presentation of the possible photoinduced processes occurring in $(\text{H}_2\text{P})_2\text{-Cu(I)}$
 $(\text{phen})_2\text{-C}_{60}$, in E-7, where $\text{L} = (\text{phen})_2$.

Table 1

Magnetic parameters of rotaxane constituents and corresponding pristine compounds.

Molecule / Moiety	Solvent	T (K)	D ^a	E ^a	A _X :A _Y :A _Z	Reference
Pristine H ₂ TPP	toluene-ethanol (1:1)	100	383	80	1:0.6:0.3	38
	E-7	100	376	75	1:0.6:0.2	22
^b Pristine C ₆₀	Toluene	116	-114	7	1:1:0	44
	E-7	163	-80	7	1:1:0	44
(H ₂ P) ₂ -Cu(I)(phen) ₂ Rotaxane	Toluene	140	374	76	1:0.5:0.2	This work
	H ₂ P	170	360	79	1:0.8:0.3	This work

^a ×10⁴ cm⁻¹; uncertainty is ±5%;

^b the magnetic parameters of ³C₆₀* for the pristine fullerene in ethanol are unavailable.