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ARTICLE

Activation Volumes Associated with Excited-State Electron Transfer Across Amidinium-Carboxylate Bridge

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Pressure was used to modulate interactions in an electron donor-acceptor system, composed of a zinc porphyrin (ZnP) and a fullerene (C₆₀), held together by an amidinium-carboxylate salt-bridge (ZnP-H⁺···C₆₀). Two different trends evolved in steady-state absorption assays. Volume compression causes an absorbance intensification, and a solvatochromic-like red shift that stems from increased E-field density. Pressure-dependent femtosecond and nanosecond transient-absorption experiments were performed to investigate the activation volumes of the excited-state deactivation processes in ZnP-H⁺···C₆₀. Solvent relaxation of S₁ was found to have a highly positive ΔV_{k2}^{\ddagger} . The pressure-induced rate attenuation for this process is assumed to be linked to the solvent's viscosity increase. Intersystem crossing to the porphyrin-centered T₁ state is free of intrinsic and extrinsic reorganizations and, as such, the activation volume is close to zero. The same applies for the subsequent ground-state deactivation from T₁ to S₀. Charge-separation to afford (ZnP)^{•+}···H⁺···(C₆₀)^{•-} is linked to a volume compression towards the activated state with $\Delta V_{k3}^{\ddagger} = -5.7 \pm 2.2 \text{ cm}^3 \text{ mol}^{-1}$. The charge-recombination undergoes, within the experimental margins of error, an equal volume expansion with $\Delta V_{k4}^{\ddagger} = +8.6 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$. This effect is linked to the generation and/or neutralization of charges, best described by the Jung equation for electrostrictive volume changes in dipolar zwitterionic entities. Importantly, volumetric contributions from a possible PT towards the activated state were not observed.

Introduction

Nature has developed various photoenergy-driven reactions that build up the world around us.¹⁻⁵ Attempts, for example, to mimic nature's light harvesting systems have received remarkable attention in recent research.⁶⁻⁹ one of the cornerstones in the pursuit of transforming our fossil fuel-based society towards renewables. Nature's sophistication in converting photoenergy to chemical fuels in photosynthesis has inspired research on porphyrins¹⁰ and porphyrinoid-based¹¹ materials and their integration into electron donor-acceptor systems.

Their capability to donate electrons in their photoexcited states renders them a perfect building block for artificial electron donor-acceptor systems. The electron acceptors of choice are

fullerenes.¹² Various compositions and configurations have been investigated over the years.¹² Bridges that connect electron donors and acceptors ranging from covalent bonds,^{13,14} and through supramolecular binding like π - π interaction,¹⁵⁻¹⁹ to neutral hydrogen bonds²⁰⁻²³ and hydrogen bonded salt bridges²⁴⁻²⁷ have been found to be important.

Electron transfer (ET) in biological systems like proteins is often coupled to a proton transfer (PT) in the hydrogen-bonded peptide environment. Leading examples are cytochrome-c oxidase in cell respiration²⁸, or photosystems I²⁹ and II^{30,31} in photosynthesis. Investigations are, however, challenging because of the complexity of the protein's structure and dynamics. Therefore, mimics have been developed and investigated to gather insight into the fundamental processes. Among others,^{21,32} the amidinium-carboxylate salt bridge stands out. Its chemical versatility, combination with a plethora of electron donors and acceptors, and its structural similarity to arginine-aspartic acid dimers in proteins, are of utmost importance.³³

The amidinium-carboxylate salt bridge was used as a blueprint to describe proton-coupled electron transfer (PCET) reactions,³⁴⁻³⁸ while they were studied with time-resolved spectroscopy experiments.^{24-26,39-42} Weak electronic couplings between the respective electron donors and acceptors, as seen in temperature-dependent transient-absorption experiments, suggests that the hydrogen-bonding interface is the bottleneck

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for electron transfer reactions.⁴³ Additionally, the orientation of the salt-bridge was identified to influence the electron transfer (ET) rate significantly. If the salt-bridge is oriented as shown in Figure 1, that is, amidinium on the electron donor and carboxylate on the electron acceptor, the electron transfer rate

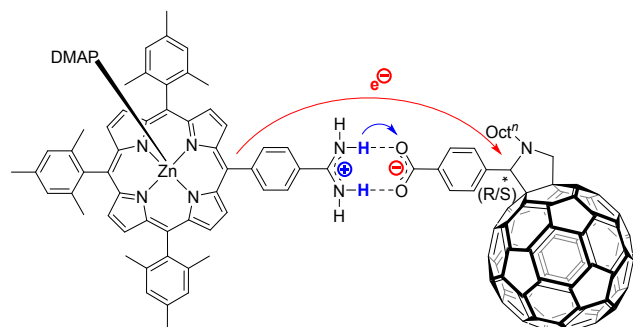


Fig. 1 Molecular structure of (ZnP-H...C₆₀): Zinc porphyrin (ZnP) connected to fullerene (C₆₀) via an amidinium-carboxylate bridge. Coordination of ZnP was saturated by addition of 4-dimethylaminopyridine (DMAP) to avoid inter-porphyrin interactions.

was attenuated compared to a hydrogen-bonded heterodimer with carboxylic acids on both the electron donor and electron acceptor.^{24,39-42} If the salt-bridge is oriented the other way round, that is, the carboxylate on the electron donor and the amidinium on the electron acceptor, a higher electron transfer rate was observed.^{24,25} The rationales for the attenuation are twofold. First, the adverse effect of the electric field across the bridge reduces the ET rate.³³ Second, a coupling between the charge-separation and -recombination rate with the bridging protons' vibrational wavefunction has been reported.⁴³ The notion of ET across the amidinium-carboxylate bridge being coupled to the proton configuration has been identified in temperature-dependent kinetic isotope effects (KIE). In particular, the thermal population of different vibrational modes alters the ET rate.^{40,42}

Questions related to any ET coupling that goes beyond the bridging proton's vibrational configuration – implying that ET is coupled to a proton transfer towards the electron acceptor – could not be finally answered.⁴³ In this notion, the photoexcitation of the electron donor, and/or the charge-separation forming to the one-electron oxidized porphyrin and one-electron reduced fullerene, are expected to come together with a significant change of the amidinium's and carboxylate's acidity/basicity properties.³³ Most of these investigations were limited by the spectroscopic features associated with the electron transfer. Proton transfer across the amidinium-carboxylate bridge is often not spectroscopically observable. It is the lack of characteristic features in the observable region that hampers an unambiguous characterization. To date, clarification of the role of the bridging protons during the charge-separation and recombination through amidinium-carboxylate salt bridges remains a challenging task. The key factor for identifying the role of the bridging proton during the observable ET has been postulated to be embodied within reorganization- and solvation free energy changes, as ET or a PCET reaction are expected to yield differently charged

products, which can be linked to differently charged intermediate states.^{35-36,43}

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According to Marcus-Hush theory, electron-transfer reaction rates k depend on both the free-energy difference ΔG^0 and the reorganization energy λ of the reactants (eq. 1). Reorganization in ET or PCET reaction is, meanwhile, best described by transition-state theory,⁴⁴ which assumes that an electron donor A and an electron acceptor B are in equilibrium with an activated complex $[AB]^\ddagger$. Charge separation proceeds from $[AB]^\ddagger$ and generates C (eq. 2). The reaction steps involved, H-bond dissociation, H-bond formation, and redistribution of electronic charges, are traceable by means of the corresponding activation volumes ΔV^\ddagger (eq. 3). ΔV^\ddagger is governed by two contributions: First, intrinsic volume changes due to contraction, expansion, and reorientation of bonds within electron donating A and electron accepting B.⁴⁵ Second, electrostrictive volume changes by reason of contraction, expansion, and reorientation of the solvation shell upon charge-separation.⁴⁶ In general, ΔV^\ddagger is a powerful tool to characterize ligand-substitution reactions in metal complexes.⁴⁷ Using ΔV^\ddagger to investigate reorganization processes has been a useful tool for characterizing ET reaction, but has found little attention for characterizing PCET reactions.⁴⁷⁻⁴⁹

$$k = A \cdot \exp\left(\frac{-\Delta G^0 + \lambda}{4\lambda RT}\right) \quad (1)$$



$$\Delta V^\ddagger = V_{[AB]^\ddagger} - (V_A + V_B) \quad (3)$$

$$\Delta V = \left(\frac{\kappa_T z^2 e^2}{8\pi\epsilon_0 \epsilon_r^2 r_i}\right) \left(\frac{\partial \epsilon_r}{\partial V}\right)_T \quad (4)$$

$$\Delta V = \left(\frac{15\kappa_T \mu_d^2}{4\epsilon_r^2 r_d^3}\right) \left(\frac{\partial \epsilon_r}{\partial V}\right)_T \quad (5)$$

In previous work, we investigated the activation volumetric effect of an excited-state PCET reaction, which took place between a non-preorganized electron donor-acceptor couple that is freely dissolved in solution.⁴⁹ In particular, we studied Haga-type $[\text{Ru}(\text{bpy})_2\text{pyimH}]^{2+}$ as an excited-state electron and proton donor, together with *N*-methyl-4,4'-bipyridinium as electron and proton acceptor in a buffered aqueous medium.⁴⁹ Any volumetric effects were treated by the Drude-Nernst expression, which describes electrostrictive volume changes that are induced by charged ions in water (eq. 4).^{46,50} In their formalism, volume changes depend on the charge of the ion sphere ze and the ion radius r_i , while compressibility of the medium κ_T , relative permittivity ϵ_r , and $(\partial \epsilon_r / \partial V)_T$ remain constant.^{46,50} Volumetric characteristics together with the Drude-Nernst relation for electrostriction effect allowed insights into the PCET mechanism, that is, a stepwise PT-ET versus a stepwise ET-PT versus a concerted process prevails.⁴⁹

Freely dissolved ions are, however, not formed upon charge-separation in covalently linked or preorganized electron donor-acceptor couples. Instead, the electron donor-acceptor couples become dipolar with zwitterionic character. Here, the Jung formalism is applicable, where volumetric changes induced by



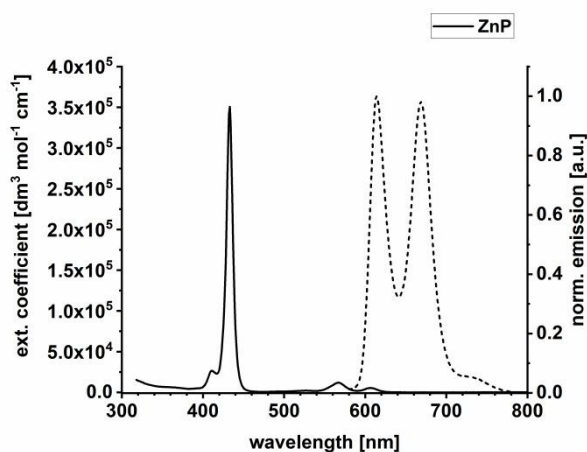


Fig. 2 Absorption (solid) and emission (dashed) spectrum of ZnP in anisole. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.

a formally spherical zwitterion depend on the radius r_d of the dipolar molecule and the dipole moment μ_d , as described in eq. 5.^{46,51} Our present work aims to test the effects described by the Jung formulation by determining the activation volumes associated with an excited-state ET reaction across an amidinium-carboxylate bridged zinc porphyrin-fullerene (ZnP-H \cdots C₆₀) couple (Figure 1). This work advances beyond our previous study, which focused on activation volume effects in independently dissolved electron donors and acceptors using Drude-Nernst theory, by investigating a preorganized electron donor-acceptor system through the Jung formalism.⁴⁹ We establish a methodology to investigate pressure-induced effects in equilibria of supramolecular complexation based on pressure-dependent steady-state absorption and emission experiments. We gather a fully-fledged description of how hydrostatic pressure influences the electronic ground and excited states of (ZnP-H \cdots C₆₀) and how pressure influences their dynamics.

Results and Discussion

Basic Characterization

Previous work on electron donor-acceptor couples featuring porphyrins (ZnP) and fullerenes (C₆₀) has shown that photoexciting ZnPs results either in an electron-transfer or an energy-transfer reaction to C₆₀.^{13,14,52,53} The solvent polarity is decisive here. In low-polarity solvents like toluene, energy-transfer dominates over electron transfer. In high-polarity solvents, electron-transfer is observed exclusively.^{13,14,52,53} Importantly, solvents of high polarity like tetrahydrofuran, benzonitrile, or dimethylformamide interfere with intermolecular hydrogen-bonds.^{10a,54} As such, we took anisole for the current studies. Anisole is sufficiently polar to direct the photoreactivity to electron transfer and allows an effective formation of hydrogen-bonded amidinium-carboxylate bridge.

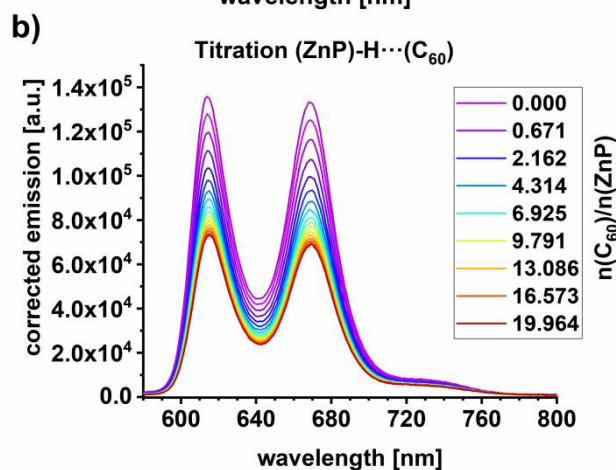
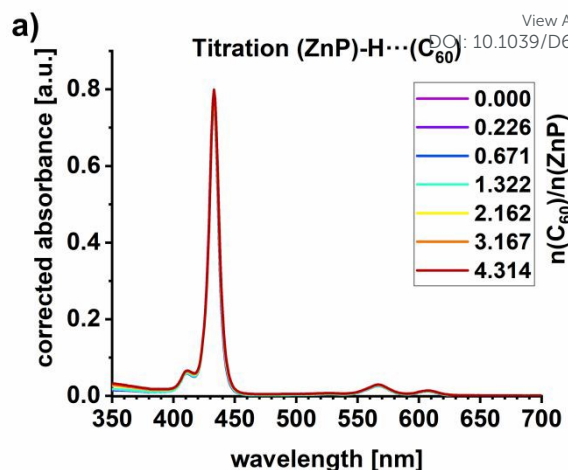


Fig. 3 a) Absorption spectra of ZnP with different amounts of C₆₀. The corresponding C₆₀ spectra were subtracted for visualization of ZnP-centered absorbance changes upon complexation. b) Fluorescence spectra of ZnP photoexcited at 567 nm with different amounts of C₆₀. Fluorescence spectra of C₆₀ were subtracted for visualization of ZnP-centered fluorescence changes upon complexation. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.

Steady-state absorption and fluorescence spectra of ZnP in anisole under ambient conditions are shown in Figure 2, while the absorption spectrum of C₆₀ is depicted in Figure S21 in the SI. For all experiments with ZnP, a 1000-fold excess of 4-dimethylaminopyridine (DMAP) was necessary to suppress any π -stacking (Figure S22 in the SI). Superimposed on the Soret-band absorption of ZnP at 432 nm (351000 dm³ mol⁻¹ cm⁻¹) is a well-defined, blue-shifted shoulder with a maximum at 411 nm. Two Q-band absorption maxima evolve at 567 nm (11900 dm³ mol⁻¹ cm⁻¹) and 607 nm (5400 dm³ mol⁻¹ cm⁻¹). The Soret-band absorption of ZnP at 432 nm is about 100-times stronger than the absorptions of C₆₀ with 4000 dm³ mol⁻¹ cm⁻¹ (Figure S21 in the SI). Hence, the Soret-band absorptions were used to photoexcite predominantly ZnP for all pressure-dependent experiments. Fluorescence maxima at 612 and 669 nm were recorded for ZnP upon photoexcitation. The ZnP fluorescence quantum yield was determined using the integrating sphere methodology resulting in values of 4.0% and 3.0% following Soret-band



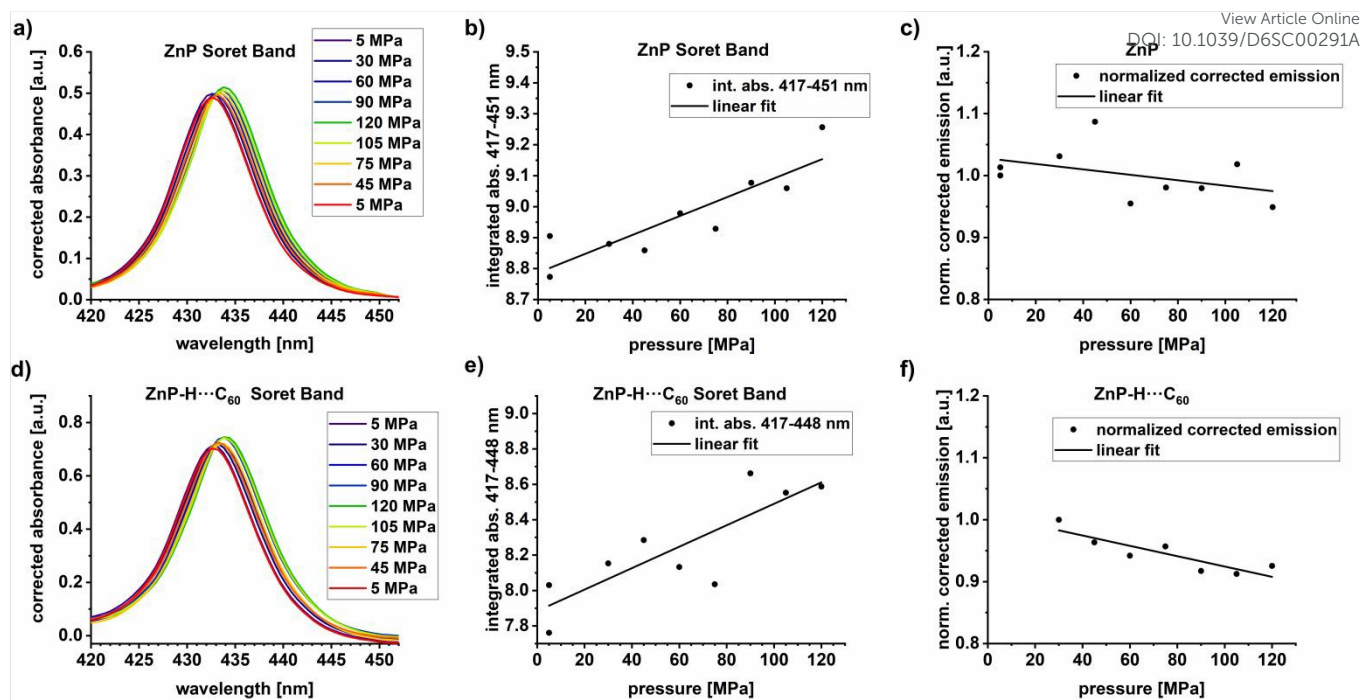


Fig. 4 a) Magnification of the ZnP Soret-band absorption in pressure dependent steady-state absorption measurements. b) Plot of integrated Soret-band absorption area vs. pressure. c) Integral of the corrected ZnP fluorescence from pressure dependent experiments using Soret band photoexcitation at 430 nm, normalized to the first data point at 5 MPa. d) Magnification of the ZnP-H...C₆₀ Soret-band absorption from pressure dependent steady-state absorption measurements, and e) corresponding plot of integrated Soret-band absorption area vs. pressure. f) Integral of the corrected fluorescence of ZnP-H...C₆₀ recorded in the pressure dependent experiments using Soret band photoexcitation at 430 nm normalized to the first data point at 30 MPa. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.

photoexcitation at 430 nm and Q-band photoexcitation at 567 nm, respectively. The fluorescence quantum yields from the two excitations are equal within experimental error.

Titration experiments were conducted to investigate the complexation of C₆₀ with ZnP (Figure 3). Only subtle changes were observed in the absorption spectra upon gradual addition of C₆₀, up to a 4-fold excess relative to ZnP. The mostly unaffected ZnP absorption is attributed to the fact that C₆₀ lacks significant impact on the electronic properties of the Franck-Condon region. Notably, the Q- and B-band transitions are primarily associated with dipole-allowed π - π^* excitations localized on ZnP. Time-dependent density functional theory (TDDFT) calculations support this interpretation (SI). Nearly identical π - π^* transitions for the ZnP Q- and B-band transitions ($S_{1/2}$: 2.16 eV; $S_{3/4}$: 3.12 eV) and ZnP-H...C₆₀ ($S_{1/2}$: 2.17 eV; $S_{3/4}$: 3.12 eV) are predicted (Figures S25–S28 in the SI). In contrast, the fluorescence gave rise to a 50% reduction in intensity (Figure 3b). We take the fluorescence quenching to indicate the presence of a new deactivation pathway in the ZnP-H...C₆₀ complex that is not present in ZnP.

Using the steady-state fluorescence titrations (Figure 3b), the binding constant was determined (Figure S23 in the SI) to be $1.9 \times 10^5 \text{ M}^{-1}$. This binding constant and the 50% reduction in fluorescence intensity are in line with previously reported data on comparable supramolecular amidinium-carboxylate salt bridged systems.⁵⁵⁻⁵⁷

Job's method of continuous variation was applied to confirm the ZnP-H...C₆₀ stoichiometry. Parabolic maximum at a molar ratio of 0.5 (Figure S24 in the SI) was identified, which confirms a 1:1 stoichiometry. Based on these results, we opted to use a 10-fold excess of C₆₀ for all further experiments, to ensure that, according to the law of mass action, at least 90% of all photoexcited porphyrins are present as ZnP-H...C₆₀, as depicted in Figure 1.

To identify the most stable configuration in solution, we performed density functional theory (DFT) calculations considering two primary conformations (SI). First, ZnP-H...C₆₀ with both bridging protons residing on the porphyrin, forming a positively charged amidinium adjacent to a negatively charged carboxylate (η^2 -binding motif between the porphyrin amidine group and C₆₀). Second, ZnP...H-C₆₀, in which the bridging hydrogen atoms are positioned on either side, forming a charge-neutral amidine-carboxylic acid bridge. DFT predicts ZnP-H...C₆₀ to be 4.31 kcal/mol more stable than in ZnP...H-C₆₀ (see Figures S29 and S30, and Tables S1–S3 in the SI).

Pressure-Dependent Absorption and Emission

To evaluate the effect of pressure, we started our investigation with pressure dependent steady-state absorption assays.⁵⁸ Our experimental setup used is described in the SI.^{49,58} We used $5 \times 10^{-6} \text{ M}$ ZnP in anisole and a 10-fold molar excess of C₆₀. Each series of measurements was conducted in the pressurization and depressurization direction to check for the reversibility of



the pressure effects. After each new pressure was set, the system was allowed to equilibrate for 15 minutes. All individual spectra were corrected by subtracting either the spectrum of the pure solvent in the ZnP experiments or that of C₆₀ in the experiments with ZnP-H···C₆₀. The full absorption spectrum under the given conditions is shown in Figure S31 in the SI. Magnifications of the Soret-band absorptions of ZnP and ZnP-H···C₆₀ are shown in Figures 4a and 4d.

Pressure induced two different effects on ZnP-H···C₆₀ and ZnP. On the one hand, absorption increases as a function of pressure, and on the other hand, a bathochromic shift from 432 to 434 nm is seen. Neither of these effects is, however, linked to any perturbations of the underlying equilibrium. Instead, we believe that they are caused by a volumetric compression and a density dependent analogue of the solvatochromic effect.^{59,60} Any volume reduction associated with increasing pressure leads to higher dielectric constants and bathochromic shifts of the S₀-S₂ transitions of ZnP.^{59,60} The low intensity/signal-to-noise ratio of the Q-band absorptions under our experimental conditions impedes any meaningful evaluation of a pressure-induced perturbation of the S₀-S₁ transition.

When analyzing the pressure dependent steady-state fluorescence data it is, however, crucial to consider the absorption intensification. The objective is to subtract any effects due to volumetric compression. We quantified the absorption intensification by linear fits ($y = a_K + b_K \cdot x$) of the integrated Soret-band absorption. In doing so, we determined the compression factor K as described in eq. 6, with the highest applied pressures ($p_{max} = 120$ MPa) and lowest applied pressure ($p_{min} = 5$ MPa for ZnP, 30 MPa for ZnP-H···C₆₀).

$$K = \frac{a_K + b_K \cdot p_{max}}{a_K + b_K \cdot p_{min}} \quad Q = \frac{a_Q + b_Q \cdot p_{max}}{a_Q + b_Q \cdot p_{min}} \quad (6)$$

The compression factor K was used to calculate the fluorescence correction factor E_i for each individual measurement i as outlined in eq.7.

$$E_i = 1 + \left(\frac{p_i - p_{min}}{p_{max} - p_{min}} \right) \cdot (K - 1) \quad (7)$$

The fluorescence intensities $I_{0,i}$, as obtained by integrating the measured fluorescence (Figures S32 and S33 in the SI), were corrected by dividing them with the fluorescence correction factor E_i and gave the corrected fluorescence intensities I_i .

$$I_i = \frac{I_{0,i}}{E_i} \quad (8)$$

The pressure induced fluorescence quenching factor Q was then calculated from the linear fits ($y = a_Q + b_Q \cdot x$) of I_i versus the applied pressure with the same procedure as used for the compression factor K , shown in eq. 6. All results for K and Q are listed in Table 1 and the corresponding plots are shown in Figure 4.

The compression factor $K = 1.04$ for ZnP represents a 4% increase of the integrated Soret-band absorption area upon increasing the pressure from 5 to 120 MPa. Correspondingly a K of 1.09 for ZnP-H···C₆₀ represents a 9% increase. The

fluorescence intensity of ZnP at 120 MPa corresponded to 95% of the intensity at 5 MPa, which relates to lower fluorescence quantum yields; 4.0% at ambient pressure versus 3.8% at 120 MPa. The emission observed for ZnP-H···C₆₀ was lowered to 90%. The slightly stronger pressure-induced fluorescence quenching in ZnP-H···C₆₀ compared with ZnP will be revisited in the discussions for the activation volumes.

Statistical noise impedes direct data interpretation. At this point, noise-correction was deemed necessary to evaluate any pressure-induced effects. We employed a multi-Gaussian fitting to model the emission spectra. The cumulated fit peaks of the multi-Gaussian fitting – Figure S35-S41 – resemble the noise-subtracted emission spectra. A closer examination of the normalized cumulative high-energy fluorescence fits reveals a pressure induced bathochromic shift of the 611.4 nm maximum at 30 MPa to 612.2 nm at 120 MPa (Figure S42). In other words, the emissive S₁-S₀ transition is also subject to a pressure-induced bathochromic shift, albeit less pronounced than the absorptive S₀-S₂ transition.^{59,60}

Transient Absorption Spectroscopy

The excited-state characteristics of ZnP and ZnP-H···C₆₀ were probed in anisole *via* femtosecond- and nanosecond transient absorption spectroscopy (fs-TAS and ns-TAS) involving photoexcitation into the Soret-band absorption at 430 nm. The fs-TAS and ns-TAS spectra of ZnP-H···C₆₀ and ZnP are shown in Figures 5 (main manuscript) and S43 (in the SI), respectively. The model used for global or target analysis is shown in Figure 6a.⁶¹ The reference experiments with ZnP were evaluated with global analysis based on a sequential four-species model without transitions k_3 and k_4 .⁶¹ These transitions were required to fit the raw data of the ZnP-H···C₆₀ in a branched target analysis model with five species.⁶¹ Corresponding evolution associated species (EAS) from global analysis of ZnP and the species associated spectra (SAS) for ZnP-H···C₆₀, together with the time-resolved population profiles are shown in Figure 6.^{61,62}

The short-lived second singlet excited state (S₂) that is populated following Soret-band photoexcitation could not be resolved fully in our pressure dependent fs-TAS. The 3 ps optical dispersion caused by the aqueous medium in the pressure cell (Figure 5) hampered its full deconvolution. Nevertheless, a fast decay corresponding to an S₂-S₁ internal conversion with a characteristic lifetime of 1.3 ps for ZnP and 1.2 ps for

Table 1 Pressure induced compression factor K and quenching factor Q from pressure dependent absorption and fluorescence experiments.

	ZnP	ZnP-H···C ₆₀
K	1.04±0.008	1.09±0.02
Q	0.95±0.04	0.90±0.03

ZnP-H···C₆₀ was required to describe the evolution of the singlet excited state (S₁) (Figure 6). Thus, the first resolved species following Soret-band photoexcitation corresponds to the ZnP-centered S₁ state. The corresponding fingerprints are



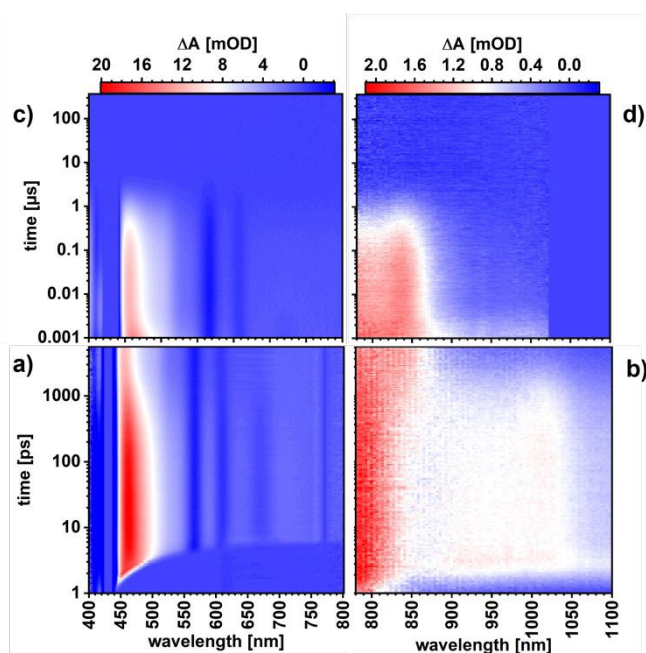


Fig. 5 fs-TAS spectra in the visible (a) and NIR region (b) of ZnP-H...C₆₀ at 5 MPa in anisole, after excitation at 430 nm with 200 nJ pulse energy. ns-TAS spectra in the visible (c) and NIR (d) under identical condition. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.

excited-state absorption (ESA) maxima at 464, 588, 639, and 707 nm, a shoulder at 535 nm next to ground state bleaching (GSB) and stimulated emission (SE) minima at 564, 614 and 668 nm (Figure 6b). This state follows a relaxation process towards the solvated singlet excited state ($S_{1,Solv}$). $S_{1,Solv}$ is discernible by a slight intensification of the 464 nm ESA maximum, which goes together with a reduction of the 464 nm full-width at half maximum (FWHM) from 53 to 50 nm. In the absence of an electron-accepting C₆₀, $S_{1,Solv}$ undergoes intersystem crossing (ISC) to afford the triplet excited state (T_1). The T_1 fingerprints are a shoulder at 502 nm in the visible region and a new ESA maximum at 838 nm, while the former SE minimum at 668 nm is diminished. T_1 deactivates to the ground state by means of oxygen quenching, as the pressure apparatus did not allow these experiments to be performed under deoxygenated conditions. When C₆₀ is present, an additional deactivation pathway from $S_{1,Solv}$ is present (Figures 6d and 6e). It competes with ISC and is identified as charge-separation that affords a charge-separated state (CSS): formation of the radical ion pair state (ZnP)^{•+}...H...C₆₀^{•-}. CSS is followed through the characteristic ESA of (ZnP)^{•+} at 415 nm,⁵⁷ while formation of C₆₀^{•-} at 1050 nm is hampered by the optical absorption of water that was used as pressure medium in the pressure cell with the 6 cm optical path length.^{14,49}

Both the lifetimes at 5 MPa and the activation volumes of the corresponding transitions are summarized in Table 2. The S_1 lifetime is 3.8 ps, while for ZnP-H...C₆₀ we observed a longer time of 7.3 ps. At this point, we are unable to explain the significantly longer lifetime of S_1 . $S_{1,Solv}$ features reveal comparable lifetimes of 1.80 ns in ZnP and 1.67 ns in

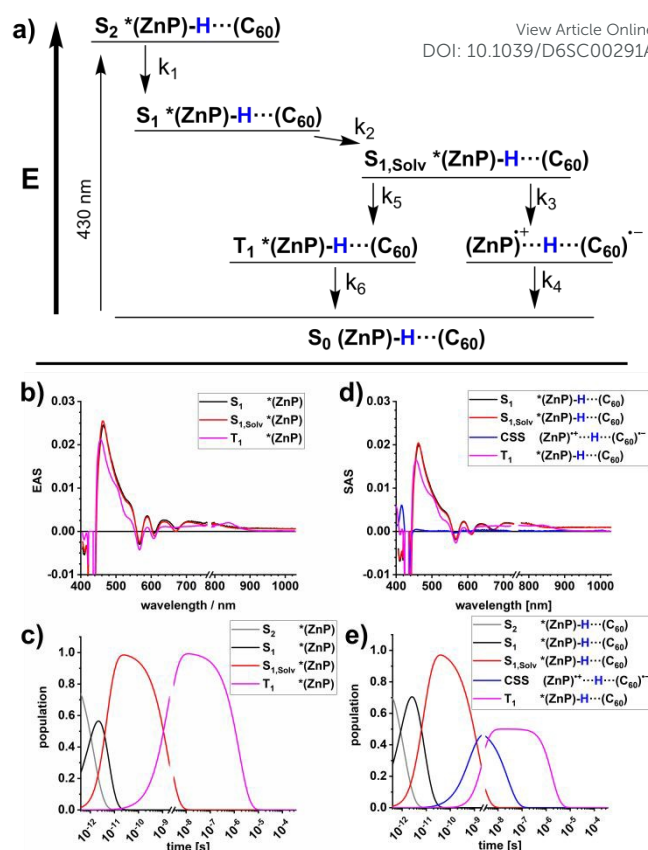


Fig. 6 a) Analysis model used for evaluating the transient-absorption spectra of ZnP and ZnP-H...C₆₀. General note: Soret-band excitation results in the initial population of S_2 . Modelling the S_2 - S_1 internal conversion was necessary for a good fit. However, the long optical dispersion through the pressure cell does not allow to assign a clear EAS or SAS for S_2 .⁶¹ b) Evolution associated spectra (EAS) from a four exponential global analysis of ZnP in anisole at 5 MPa.⁶¹ c) Time profiles depicting the time-resolved population of the corresponding EAS of ZnP from global analysis.^{61,62} d) Species associated spectra (SAS) from branched six exponential target analysis of ZnP-H...C₆₀ in anisole at 5 MPa.^{61,62} e) Time profiles depicting the time-resolved population of the corresponding SAS of ZnP-H...C₆₀, from target analysis. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.^{61,62}

ZnP-H...C₆₀. The same applies for the subsequently formed T_1 , which decays with 1.61 or 1.82 μ s, respectively. The $S_{1,Solv}$ state lifetime, which reflects the charge-separation to generate (ZnP)^{•+}...H...C₆₀^{•-}, is much shorter with 634 ps. The lifetime of CSS is 25.1 ns, during which the singlet ground state (S_0) is recovered by means of charge-recombination.

Activation Volumes

Insights into activation volumes ΔV^\ddagger that correspond to these processes come from investigating the reaction kinetics k as a function of pressure p , as described by the Maxwell relation in eq. 9. We determined the activation volumes by performing fs-TAS and ns-TAS experiments under pressure. ΔV^\ddagger values were calculated as described in the SI.⁴⁹ The slopes of the $\ln(k)$ - p plots for ZnP-H...C₆₀ are shown in Figure 7, and those for ZnP in Figures S48-S51. All relevant ΔV^\ddagger values are listed in Table 2. The initial process in fs-TAS, the S_2 - S_1 transition, is linked to a

$$\frac{\delta \ln k}{\delta p} = \frac{-\Delta V^\ddagger}{RT} \quad (9)$$



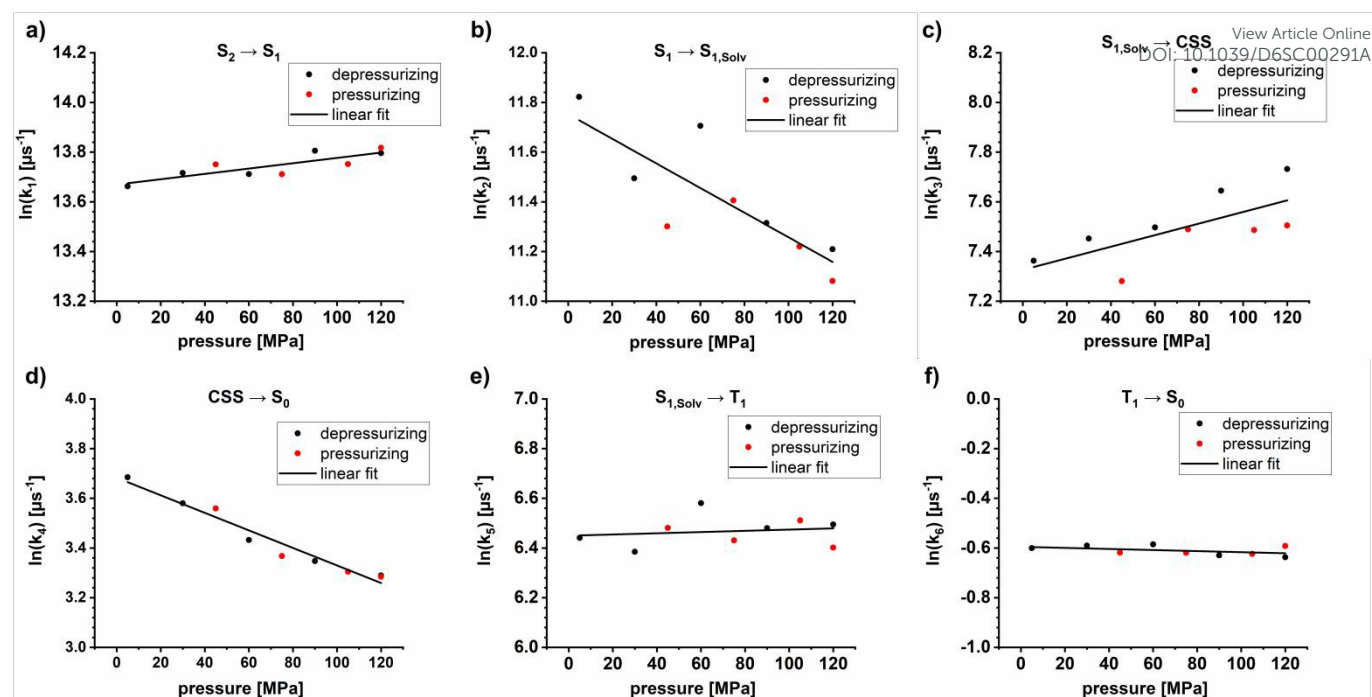


Fig. 7 a) Pressure effect on the reaction rate k_1 of ZnP-H...C₆₀ for S₂-S₁ conversion b) Pressure effect on k_2 , associated with solvent relaxation from S₁ to the solvated S_{1,Solv}. c) Pressure effect on k_3 , associated with the charge-separation from S_{1,Solv} towards the charge-separated state (CSS). d) Pressure effect on k_4 , associated with the charge-recombination from CSS to S₀. e) Pressure effect on k_5 , associated with the intersystem crossing from S_{1,Solv} towards T₁. f) Pressure effect on k_6 , associated with the ground-state deactivation by means of oxygen quenching from T₁ to S₀. A 1000-fold excess of DMAP vs. ZnP was used in all optical spectroscopy experiments.

slightly negative ΔV_{k1}^\ddagger (Figures 7a and S48 in the SI). However, the 3 ps optical dispersion failed to capture S₂ following photoexcitation into the Soret-band absorption fully – *vide supra*. Consequently, an unambiguous interpretation of the effects observed is not possible. A positive ΔV_{k2}^\ddagger of more than +10 cm³ mol⁻¹ (Figures 7b and S49 in the SI) was determined for the subsequent solvent-relaxation process to yield S_{1,Solv}. This corresponds to a significant rate deceleration as the pressure is increased. We link this effect to the pressure-induced increase in solvent viscosity.⁵⁹ The spectral features of S₁ and S_{1,Solv} differ, however, only marginally (Figures 6b and e). This challenges the interpretation of any observable pressure-induced effects. ISC from S_{1,Solv} to T₁ is an activation volume-free process, with ΔV_{k5}^\ddagger values close to zero (Figures 7e and S50 in the SI). It is porphyrin-centered and not subject to a change in charge density. As such, the intrinsic reorganization should be low and the influence on the solvation shell should be subtle. Deactivation to the ground state should also occur activation volume-free with ΔV_{k6}^\ddagger close to zero (Figure 7f and S51 in the SI).

Charge-separation in ZnP-H...C₆₀ occurs with a negative ΔV_{k3}^\ddagger of -5.7 ± 2 cm³ mol⁻¹, while charge-recombination has a comparable but positive ΔV_{k4}^\ddagger of $+8.6 \pm 0.7$ cm³ mol⁻¹ (Figures 7c and 7d). A negative activation volume is a result of a pressure-induced acceleration of the charge-separation. This is in accordance with the pressure-induced fluorescence quenching seen for ZnP-H...C₆₀ (Figure 4f and Table 1). An accelerated charge-separation

leaves a lower ratio of photoexcited ZnP to undergo fluorescent decay.

The following factors are considered to evaluate the mechanistic implications of ΔV_{k3}^\ddagger and ΔV_{k4}^\ddagger . First, ZnP and C₆₀ are rigid in nature.⁶³ As such, significant bond-length alterations within these electron donors and acceptors are ruled out. A reorganization within the amidinium-carboxylate bridge in the activated state by means of, for example, a proton transfer would result in a neutralization of the charges and to weaker attractive forces across the bridge.^{24,41} One might expect, at this point, longer N...H...O bond lengths with positive activation volumes. Neutralization of charges across the amidinium-carboxylate bridge implies a lower dipole moment μ_d , which is well treated the Jung expression (eq. 5), and which leads to a volume expansion of the solvation shell.^{46,51} This conflicts, however, with the negative activation volumes seen in the experiments for ΔV_{k3}^\ddagger . Instead, the volume reduction *en route* to the CSS is likely associated with any of the two following factors. First, oxidation of the porphyrin is linked to a lower electron density at the Zn-center and, in turn, a higher affinity to DMAP as donor ligand. The net effect would be a ZnP-DMAP bond length contraction. Second, charge-separation is linked to the formation of the one-electron oxidized form of the porphyrin and the one-electron reduced form of C₆₀. Considering that electrostrictive volume differences and radii of the dipolar moiety r_d are inversely proportional to each other, both hypothetically possible reactions, that is, formation of charged ZnP and C₆₀ and charge-neutralization within the



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Table 2 Lifetimes at 5 MPa and activation volumes from pressure-dependent transient absorption experiments.

System	Lifetimes						Activation Volumes [cm ³ mol ⁻¹]					
	S ₂ τ ₁ [ps]	S ₁ τ ₂ [ps]	S _{1,Solv} τ ₃ [ps]	CSS τ ₄ [ns]	S _{1,Solv} τ ₅ [ns]	T ₁ τ ₆ [μs]	S ₂ -S ₁ ΔV _{k1} [‡]	S ₁ -S _{1,Solv} ΔV _{k2} [‡]	S _{1,Solv} -CSS ΔV _{k3} [‡]	CSS-S ₀ ΔV _{k4} [‡]	S _{1,Solv} -T ₁ ΔV _{k5} [‡]	T ₁ -S ₀ ΔV _{k6} [‡]
ZnP	1.3	3.8	–	–	1.80	1.61	-3.1 ± 0.6	+26 ± 3	–	–	0.0 ± 0.3	-1.9 ± 1.0
ZnP-H···C ₆₀	1.2	7.3	634	25.1	1.67	1.82	-2.6 ± 0.6	+12 ± 3	-5.7 ± 2	+8.6 ± 0.7	-0.6 ± 1.4	+0.5 ± 0.4

amidinium-carboxylate bridge, contribute to the observable activation volumes. Oppositely charged ZnP and C₆₀ create a dipole moment and, in turn, increase the electrostriction.^{46,51} Stronger interactions with the solvent dipole moments is the direct consequence and this leads to a volume compression following the Jung equation (eq. 5).^{46,51} If both charge-carriers are transferred in a single kinetic step, as, for example, *via* a PCET reaction the opposing volumetric effects will balance out and activation volumes will be negligible.⁴⁹ Considering these contributions in concert, we conclude that the transition state of charge-separation across the amidinium-carboxylate bridge is dictated exclusively by electron transfer. Herby, the charge-separated state (ZnP)^{•+}···H···(C₆₀)^{•-} is formed without any detectable volumetric contributions stemming from a proton transfer across the amidinium-carboxylate bridge.

The same arguments are applicable for the charge-recombination. Any increase in electron-density at the ZnP-core leads to a lower DMAP affinity and to a ZnP-DMAP bond elongation. Additionally, the neutralization of the opposite charges at the ZnP and C₆₀, that is one-electron oxidized and reduced forms, lowers the previous electrostriction and interactions with the solvent dipole moments as described by the Jung equation.^{46,51} Both effects result in the observable positive activation volume ΔV_{k4}[‡]. Consequently, effects from a transfer of electrons also govern the activated state as the bottleneck in charge-recombination. Volumetric contributions from a proton transfer remain non-observable.

Summary

A supramolecular electron donor-acceptor system, consisting of trimesitylene-phenylamidinium-zinc porphyrin (ZnP) as electron-donor and *n*-octyl-fulleropyrrolidine-benzoic acid (C₆₀) as electron-acceptor, was synthesized. Studies necessitated a 1000-fold excess of DMAP to avoid intermolecular ZnP π-stacking. DFT calculations suggest that these building blocks form a charged η²-binding motif in their ground state, in which both bridging H-atoms are located at ZnP.

Steady-state experiments unveiled a 1:1 stoichiometry with a binding constant of 1.9 × 10⁵ M⁻¹. In the steady-state absorption experiments, two pressure-induced effects were seen. On one hand, an increase in optical density is linked to a volume compression. On the other hand, a bathochromic shift of the absorption is due to an increasing dielectric constant. Fluorescence experiments similarly showed a subtle bathochromic shift together with a small pressure-induced quenching for ZnP-H···C₆₀ compared to ZnP.

Pressure-dependent fs-TAS and ns-TAS were carried out to investigate the activation volumes (ΔV[‡]) of the excited-state deactivation in ZnP-H···C₆₀. S₂, which was populated through photoexcitation into the Soret-band absorption, could not be fully registered due to the 3 ps optical dispersion. Transition from S₁ towards S_{1,Solv} has a highly positive activation volume. The underlying rate attenuation is linked to a pressure induced viscosity increase. ISC to yield T₁ and subsequent ground-state deactivation to S₀ are free of any molecular reorganization and the corresponding activation volumes are essentially zero. Charge-separation is linked to a negative activation volume of -5.7 ± 2 cm³ mol⁻¹. Charge-recombination has a comparable, but positive activation volume of +8.6 ± 0.7 cm³ mol⁻¹.

Pressure-dependent reaction kinetics were used to investigate intrinsic as well as electrostrictive volume effects for charge-separation and -recombination in a ZnP-H···C₆₀ system across an amidinium-carboxylate bridge, by using the Jung equation for dipolar molecules. Volumetric effects in the activated states for either charge-separation or -recombination are mostly determined by electron transfer. Volumetric contributions from a proton movement are non-observable. Consequently, both activation volumes are determined by electron-transfer processes, while effects induced by a proton-transfer during charge-separation and -recombination are absent.

Our presented work highlights the possibility of using pressure-dependent reactions kinetics to investigate the intrinsic and electrostrictive volume effects in pre-organized electron donor-



acceptor systems. This extends our previously reported scope of high-pressure kinetics for studying charge-separation and -recombination reactions based on the Drude-Nernst theory for freely-dissolved reactants to covalently/non-covalently pre-organized electron donor-acceptor systems forming dipolar zwitterions as intermediates, based on the Jung theory.⁴⁹⁻⁵¹

Conclusions

The activation volumes of the observable electron transfer between ZnP and C₆₀ across an amidinium-carboxylate bridge occur without any volumetric contributions from a proton transfer within the bridging unit towards the formation of the respective activated states. Congruently, the transition states of charge-separation and -recombination are determined by contributions from electron rather than proton transfer.

Author contributions

D.L. conducted complexation experiments by means of steady-state absorption and emission spectroscopy. D.L. conducted pressure dependent experiments by means of steady-state absorption, emission, fs- and ns-TA experiments. D.L. main-authored the manuscript. R.W., M.K., C.M. and T.C. contributed with theoretical calculations. R.W. co-authored the manuscript. M.U. synthesized the investigated compounds and characterized them with NMR, MALDI-TOF, ESI-TOF, UV-Vis and fluorescence. M.U. co-authored the manuscript. A.Z. contributed with technical support for the pressure equipment. T.T. and D.M.G. conceived the project and co-authored the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. See DOI: [https://doi.org/DOI].

Data for this article, including ambient pressure steady state absorption and emission, pressure-dependent steady state absorption and emission, and pressure-dependent transient absorption data are available at Zenodo at <https://doi.org/10.5281/zenodo.18648422>.

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Data availability

The data supporting this article have been included as part of the Supplementary Information. See DOI: [https://doi.org/DOI]. Data for this article, including ambient pressure steady state absorption and emission, pressure-dependent steady state absorption and emission, and pressure-dependent transient absorption data are available <https://doi.org/10.5281/zenodo.18648422>.

