Screening Nanographene-Mediated Inter(Porphyrin) Communication to Optimize Inter(Porphyrin–Fullerene) Forces

Philipp Haines, Ramandeep Kaur, Max M. Martin, Martin B. Minameyer, Stefan Frühwald, Simon Bönisch, Dominik Lungerich, Frank Hampel, Andreas Görling, Thomas Drewello, Norbert Jux, and Dirk M. Guldi*

1. Introduction

Porphyrin–fullerene electron donor–acceptor systems have been at the focal point of studies in recent decades.[1–6] Constituting a suitable platform for interdisciplinary investigations regarding energy and electron transfer reactions, numerous studies on covalent and noncovalent interactions fostered our understanding to replicate key aspects of natural photosynthesis.[7] Linking porphyrins and fullerenes covalently not only secures sufficient electronic coupling between them to power, for example, electron transfer, but also to fine-tune it by choosing the right molecular bridge.[8,9] A major drawback of linking them is the need of functionalization that alters their physicochemical properties.

Solution-based investigations on noncovalently interacting porphyrins and fullerenes have, however, to overcome the weak interactions between the curved and the planar molecules. Multifunctional molecular materials comprising porphyrins and fullerenes have served as perfect prototypes to study key aspects of natural photosynthesis starting at light harvesting and energy transfer processes all the way to charge separation, charge shift, and charge recombination. Herein, hexa-peri-hexabenzocoronenes (HBCs) are explored, decorated with one, two, and six porphyrins at their peripheral positions, within the context of replicating key steps of photosynthesis. The major focus of the investigations is to screen inter(porphyrin) communications across the HBC platform as a function of the substitution pattern and to optimize the intermolecular forces with fullerenes. To this end, the ground- and excited-state features are investigated in the absence of C60 and C70 by employing an arsenal of spectroscopic methods. Further insights into inter(porphyrin) communications come from time-dependent density-functional theory (TDDFT) calculations. In the presence of C60 and C70, X-ray crystallography, steady-state and time-resolved spectroscopy, and mass spectrometry corroborate exceptionally strong inter(porphyrin–fullerene) interactions in the solid, liquid, and gas phases. The experiments are backed-up with DFT calculations of the geometrically optimized and energetically stable complex configuration.
flat π-surfaces of fullerenes and porphyrins, respectively. Consequently, early studies focused majorly on probing noncovalent interactions between porphyrins and fullerenes in cocrystals.\(^{[10,11]}\) In the solid state, porphyrins and fullerenes attract each other via π–π interactions supplemented by electrostatic and/or charge transfer interactions.\(^{[12,13]}\) In solution, however, alternative strategies are considered to realize an efficient and selective binding. For example, rendering the porphyrins more electron-rich and/or the fullerenes more electron-deficient as well as incorporating suitable building blocks are all powerful means to optimize intermolecular forces.\(^{[14,15]}\) Yet, another potent strategy is based on the structural control over multiporphyrinic binding sites, which are specifically designed to host fullerenes in an efficient and selective manner.\(^{[7,16–19]}\)

As a suitable platform for forming multiporphyrinic binding sites, hexa-peri-hexabenzocoronenes (HBCs), to whose peripheral positions porphyrins are attached, stand out. HBC, as one of the smallest members, belongs to the family of nanographenes, an interesting class of molecular materials, which combine the synthetic and photophysical versatility of smaller graphenes, an interesting class of molecular materials, which facilitate the HBC–porphyrins (Figure 1) to advanced steady-state and time-resolved spectroscopic methods. Importantly, the results were complemented by DFT calculations.

### 2. Steady-State Characterization of Inter(Porphyrin) Interactions

With focus on unraveling interporphyrinyl communication in the ground state, we inspected the absorption spectra of 1, 2o, 2m, 2p, and 6. The absorptions of all HBC–porphyrin conjugates exhibit features stemming from HBCs and ZnPs, namely, the β and p-bands, on the one hand, and the Soret- and Q-bands, on the other hand. Notably, the symmetry-forbidden α-bands of HBCs, which are weakly allowed due to symmetry lowering, peripheral-positioned ZnPs, are covered by the intense Soret-bands of the ZnPs.

HBC features are discernable for 1 at 343, 359, and 387 nm (Figure 2; Figure S1, Supporting Information). Compared to 2,5,8,11,14,17-hexa-tert-butyl-hexa-peri-hexabenzocoronene (HBC-tBu), the absorption features of 1 are, however, hypochromically shifted by 1–2 nm. Even stronger are the blue-shifts for 2o, 2m, and 2p.

ZnP Soret-band features appear for 1 at 432 nm with an extinction coefficient of \(4.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\). They are broadened, weakened, and redshifted, relative to the 423 nm maximum for the 5,10,15,20-tetraphenylporphyrinato-zinc(II) (ZnP) reference with \(5.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\). For 2o, 2m, and 2p, they further broaden and, most importantly, split. Very prominent are these changes in 2p. The Soret-band split in 2o results in a major maximum and a minor one at 428 and 437 nm, respectively. For 2m, the major maximum shifts to 429 nm and the minor...

---

**Figure 1.** Structures of monosubstituted (1), ortho-disubstituted (2o), meta-disubstituted (2m), para-disubstituted (2p), and hexa-substituted, (6) HBC–porphyrins.
maximum at 437 nm becomes far more noticeable. For 2p, the ratio is reversed with the 437 nm maximum that dominates over the 429 nm maximum. Even stronger is the Soret-band split for 6 with two major maxima at 424 and 437 nm. Despite the fact that the number of ZnPs is up to six times higher relative to 1, the extinction coefficients are, for example, for the Soret-band absorptions in the range from $5.0 \times 10^5$ to $7.0 \times 10^5$ m$^{-1}$ cm$^{-1}$ for 6 and 2o, respectively (Figure 2). Only a marginal impact on the location and shape of the Q-band features is seen for 2o, 2m, and 2p. Common to all of them is that they are 2 nm redshifted and accompanied by a third Q-band absorption at 639 nm. [38]

Broadening and bathochromic shifting of the ZnP-centered absorptions in all HBC–porphyrin conjugates stem from sizeable ground-state interactions and/or degeneracy breaking of the molecular orbitals. Due to their larger transition dipole moments, the Soret-band transitions are far more susceptible to changes than the Q-band absorptions. To this end, the Soret-band split in the regioisomeric 2o, 2m, and 2p is rationalized on the grounds of the nature of interactions between the ZnPs. The low-energy Soret-band absorption arises from interporphyrinic electron–vibration couplings, which are enabled by the $\pi$-conjugation across the HBC platform. The different oscillator strengths, which are weakest in 2o and strongest in 2p, define the extremes of the interaction scale. The high-energy Soret-band transition is solely located on a single ZnP.

Support for these conclusions came from TDDFT calculations of the natural transition orbitals (NTOs) of the Soret-band transitions. [39] We tested 1, 2o, 2m, and 2p. The calculated spectra (Figure 3) match qualitatively the experimental spectra (Figure 2), although the intensity of the low-energy Soret-band transition is more intense and all maxima are 40 nm blueshifted. Most important are the facts that the Soret-band splits into two maxima around 380 and 395 nm with relative ratios depending on the respective regioisomer.

The nature of the Soret-band splits is unraveled by a closer look at the occupied and virtual NTOs. Depending on the regioisomer and the excitation energy, the NTOs are either delocalized on both porphyrins or localized on one of them. Here, the results provide valuable insights into the localized and delocalized nature of the high- and low-energy Soret-band maxima, respectively. For example, the NTO of 2p with the largest contributions of the high-energy Soret-band (378 nm) displays a localization on one ZnP, while the respective NTO of the low-energy Soret band (392 nm) is delocalized over the entire molecule (Figure 4). Similar results were found for 2o and 2m. [40]

To get a closer look on interporphyrinyl interactions in the excited state, 3D fluorescence heat maps were recorded (Figure 5; Figure S38, Supporting Information). Exciting into the HBC features leads to a strongly quenched HBC fluorescence in the 500 nm range. The quenching scales with the number of attached ZnPs. Recording, instead, the strong ZnP-based fluorescence with maxima at 601/602 and 648 nm indicates an efficient and unidirectional energy transfer from HBC to the ZnPs. Notably, the $0–1$ transitions are more prominent in 2o and 6, which prompts to interporphyrin communications caused by the close proximity between the individual ZnPs.

Similar are the conclusions stemming from the fluorescence quantum yields. These were determined in toluene, where a value of 3.3% was determined for the ZnP reference (Table S3 and Figure S39, Supporting Information). 1 and 2p exhibit even higher fluorescence quantum yields of 5.5% and 5.6%, respectively. Slightly lower are the values for 2m and 2o with 5.3%. 6 shows the lowest values of 5.0%. Our results exemplify the effects,
which stem from inter(porphyrin) stacking, and, which are particularly strong in 6, as determined from its crystal structure.[30,41]

3. Time-Resolved Characterization of Inter(Porphyrin) Interactions

Next, all HBC–porphyrin conjugates were subjected to transient absorption measurements using two different excitation wavelengths, that are, 387 and 430 nm. All conjugates exhibit characteristic ground-state bleaching concurrent with new transients across the visible and near-infrared regions. We employed global and target analyses as tools to deconvolute the spectral evolution as a function of time.

Firstly, we inspected 1 in benzonitrile upon excitation with 387 nm. 1 displays an intense ground state bleaching at 439 nm next to positive transients at 466, 542, 620, 702, 800, 948, and 1400 nm (Figure S41, Supporting Information). At first glance, the instantaneously formed excited-state features of 2o, 2m, and 2p differ from those recorded for 1 only with respect to the strong Soret-band split. The high- and low-energy Soret-band bleaching at 429 and 442 nm, respectively, and their ratios differ in each dimer. For example, the ground state bleaching at 429 nm is far more intense in 2o than it is at 442 nm. Notable is the fact that the kinetics differ; they are slower at 429 nm than at 442 nm (Figure S45, Supporting Information). In difference to 2o, the intensity of both bleaching is more or less the same in 2m. However, in the 2m case, the kinetics of 429 nm are faster than those at 442 nm (Figure S49, Supporting Information). In 2p, the bleaching at 429 nm is less intense than that at 442 nm (Figure S53, Supporting Information). The decay at the 429 nm bleaching is, however, faster. The excited state features of 6 strongly resemble the excited state features of 2m with minor changes in the energetic location of the spectral features (Figure S57, Supporting Information).

To fit the raw-data for 1, we applied a sequential model based on three species in the target analysis (Figures S42 and S61, Supporting Information). We assign the first species, which is (2.8 ps)-lived, to an HBC-centered singlet excited state. It undergoes a transfer of energy to ZnP. Importantly, the excited-state features at 542 and 620 nm match perfectly the singlet excited state features seen for HBCs. On the one hand, the blue- and redshifts of these features and, on the other hand, the simultaneous growth of the ZnP-related features at 439 and 466 nm corroborate the energy transfer postulate. The correspondingly formed ZnP singlet excited state is the second species. Population of a higher lying ZnP singlet excited state is the second species. Population of a higher lying ZnP singlet excited state, which is highly likely, cannot be confirmed in our experiments. It is important to note that the internal conversion is with a lifetime as short as 0.6 ps—vide infra—faster than the 2.8 ps energy transfer. In other words, a higher lying ZnP...
singlet excited state decays faster than formed. The second species decays in 1.7 ns to yield the third species.\[42\] The triplet excited state and ground state recovery is completed within 274 \( \mu s \).

For \( 2o \), \( 2m \), and \( 2p \), four rather than three species were needed in a sequential model to fit the raw data. The HBC-to-ZnP energy transfer, which links the first species with the second species, is substantially faster due to the stronger electronic interactions between HBC and the multiple ZnP's (Table S5 and Figures S46, S50, and S54, Supporting Information; Figures 6 and 7). Once again, it is the ZnP singlet excited state rather than a higher lying ZnP singlet excited state that is the product of the transduction of energy. In contrast to 1, an additional process follows the conclusion of the energy transfer before intersystem crossing drives the triplet excited state formation. Lifetimes for this process are on the order of tens of picoseconds. Considering that the low-energy Soret-band bleaching at 442 nm is reinforced, we assign this process to a transformation of a localized ZnP singlet excited state into a delocalized ZnP singlet excited state.\[43–45\] This yields the third species.\[46,47\] From this delocalized and structurally relaxed singlet excited state, the \( 2o \), \( 2m \), and \( 2p \) deactivations resemble that concluded for 1. In particular, the nanosecond decay affords predominantly the evolution of the localized triplet excited state as the fourth species.\[48–52\] It takes hundreds of microseconds to deactivate the latter and to reinstate quantitatively the ground state.

The excited-state dynamics for 6 differ as no evidence for any HBC-to-ZnP energy transfer was found. This is in sound agreement with the steady-state absorption.\[30\] Implicit is that as the number of ZnP's increases perturbation of the electronic structure of HBC starts to dominate. Accordingly, we revised the kinetic model in the target analysis (Table S5 and Figures S58 and S62, Supporting Information; Figure 6). Instead of an energy transfer, a 0.4 ps lasting relaxation by means of internal conversion of a ZnP-centered higher lying singlet excited state is seen. Excited state localization of this relaxed state goes hand-in-hand with an intensification of the blue-part of the Soret-band absorption. In 9.3 ps, an initial delocalization with, for example, neighboring ZnP's in ortho-, meta- or para-position, leads to a

---

**Figure 6.** Transient absorption spectra (left) of \( 2o \) recorded at 387 nm photoexcitation in the visible and near-infrared regions with time delays between 0 and 5500 ps in Ar-saturated benzonitrile. Species associated spectra (SAS) and corresponding population profiles of \( 2o \) in benzonitrile upon photoexcitation at 387 nm (right) with time delays between 0 to 5500 ps. The deconvoluted SAS correlate with the following species: SAS1 in dark blue—HBC-centered singlet excited state; SAS2 in green—ZnP-centered singlet excited states; SAS3 in red—delocalized ZnP-centered singlet excited state; SAS4 in brown—ZnP-centered triplet excited state.

**Figure 7.** Left: Deactivation schemes of the excited-state dynamics for \( 2o \), \( 2m \), \( 2p \) upon photoexcitation at 387 and 430 nm. The species associated spectra (SAS) deconvoluted for the 387 nm measurements correlate with the following species: SAS1 in dark blue—HBC-centered singlet excited state; SAS2 in green—ZnP-centered singlet excited states; SAS3 in red—delocalized ZnP-centered singlet excited state; SAS4 in brown—ZnP-centered triplet excited state. Please note that the dashed black line, namely the ZnP-centered second singlet excited state, implies that the energy transfer from the HBC-centered singlet excited state to the ZnP-centered second singlet excited state is slower than the internal conversion and, in turn, cannot be deconvoluted. Right: Deactivation schemes of the excited-state dynamics for 6 upon photoexcitation at 387 and 430 nm. The species associated spectra (SAS) deconvoluted for the 387 nm measurements correlate with the following species: SAS1 in dark blue—HBC-centered singlet excited state; SAS2 in green—ZnP-centered singlet excited state; SAS3 in yellow and SAS4 in red—delocalized ZnP-centered singlet excited state; SAS5 in brown—ZnP-centered triplet excited state. Please note that the dashed black line, namely, the ZnP-centered second singlet excited state, implies that the energy transfer from the HBC-centered singlet excited state to the ZnP-centered second singlet excited state is slower than the internal conversion and, in turn, cannot be deconvoluted.
change of the Soret-band bleaching, that is, the red—rather than the blue-pair intensities. From here, another delocalization, which takes 191 ps, is observed. We hypothesize such a transformation is a singlet excited state delocalization/depolarization over all six of the ZnP. Like what is seen in 2o, 2m, and 2p, the delocalization/depolarization is followed by ground-state recovery and the population of the localized triplet excited state. In other words, the fourth and fifth species are the first delocalized singlet excited state and the triplet excited state, respectively.

Photoexcitation at 430 nm leads to similar results, but without forming any HBC-centered singlet excited state and without any HBC-to-ZnP energy transfer. Instead, the ZnP are directly excited to afford a higher lying singlet excited state (Figure 7; Figures S43, S44, S47, S48, S51, S52, S55, S56, S59, S60, and S61, Supporting Information). Relaxations via internal conversion take place between 0.6 and 1.5 ps in benzonitrile as well as between 1.2 and 2.2 ps in toluene. Next, delocalization of the ZnP singlet excited state and/or rotational relaxation forms the structurally relaxed, delocalized ZnP singlet excited state. This is followed by intersystem crossing and ground-state recovery. The lifetimes of the rotational relaxation upon 430 nm ZnP photoexcitation are notably shorter than those upon 387 nm HBC photoexcitation. They follow, however, the same trend (Table S6, Supporting Information).

4. Steady-State and Time-Resolved Characterization of Inter(Porphyrin–Fullerene) Interactions

After elucidating the ground- and excited-state reactivities of, 1, 2o, 2m, 2p, and 6, we shifted our focus toward interactions with fullerenes. To this end, we explored some of them in combination with C60 and C70 in three different phases: solid, solution, and gas.

4.1. Solid-Phase Inter(Porphyrin–Fullerene) Forces

Crystals, suitable for X-ray diffraction experiments, were grown by preparing either benzene or toluene solutions of the respective HBC–porphyrin conjugates. An excess amount of a saturated C60 solution in the same solvent was added. The mixed solutions were carefully overlaid with methanol and stored light-protected at room temperature for several weeks. Following this procedure, C60@2o and C60@2pH2 (free-base porphyrin of 2p) cocrystals were obtained. The data complements the solution- and gas-phase experiments—vide infra—and allows an insight into inter(porphyrin–fullerene) interactions in the solid state.

C60@2o cocrystals show a perfect size correlation between 2o as host and C60 as guest (Figure S62a, Supporting Information) that enables strong supramolecular interactions. As already observed for previously reported HBC–porphyrin conjugates,[26–28,30] C60@2o with its 1:1 stoichiometry gives rise to dimeric pairs, which are driven by attractive π–π interactions between the HBC planes as the major packing motif (Figure S62 b,c, Supporting Information). Although 2pH2 lacks an apparent cavity, the cocrystal structure revealed that each fullerene is complexed by two individual 2pH2s via attractive π–π interactions (Figure 8a). This leads to the formation of 1D, noncovalently linked electron donor–acceptor wires within the crystal (Figure 8b). Additional details are shown Table S7 and Figure S63 (Supporting Information).

4.2. Solution-Phase Inter(Porphyrin–Fullerene) Forces

Motivated by the promising results in the solid state—vide supra—we placed our focus onto interactions in solution. Addition of increasing amounts of C60 or C70 to a solution of 2o leads to changes in the absorption and fluorescence features of the latter. In particular, the ZnP-based absorptions exhibit shifts in C60@2o, which indicate interactions of C60 or C70 with the ZnP of, for example, 2o. With an increase in C60 or C70 concentrations the Soret-band absorption redshifts by 5 nm and deintensifies (Figure 9; Figures S64 and S65, Supporting Information). The same trend emerges in terms of the Q-band absorptions. Here, 1.5 nm redshifts are noted. The former goes hand-in-hand with a fluorescence quenching for 2o that amounts to ~70% and ~95% in the cases of C60 and C70, respectively. Based on a nonlinear fitting function the binding constants for C60@2o and C70@2o were determined as 2.6 × 105 and 1.1 × 106 M−1, respectively.

In C60@6, the effects are even stronger (Figure S66, Supporting Information). The split Soret-band absorptions redshift with the high-energy one shifting stronger than the low-energy one, that is, 5–7 nm versus 2 nm. Subtle is, however, the redshifting of the Q-band absorptions. Overall, titrations of 6 with C60 lead to much firmer changes than with C60 (Figure 10; Figure S67, Supporting Information). At a 7:1 stoichiometry of C70@6, the fluorescence of 6 is quenched by more than 95%. The same quenching is realized for C60@6 at, however, a 30:1 ratio. Following the binding constant determination, which was applied.
for C_{60}²o, afforded exceptionally high values of $4.8 \times 10^6$ and $8.7 \times 10^6$ m\(^{-1}\) for C_{60}⁶ and C_{70}⁶, respectively (Figures S66 and S67, Supporting Information). Considering the multiple C_{60} and C_{70} bindings by 6, it is, however, impossible to follow each complexation step. Most notable are rationales such as solubility, instrumental limitation, etc.\(^{[53]}\)

Next, our probe was electron or energy transfer in C_{60}²o and C_{60}⁶ by transient absorption spectroscopy. Upon their photoexcitation at 430 nm, the immediate formation of ZnP-based excited state transients and ground-state bleaching in the visible region were noticeable. Within 10–14 ps, the latter transformed into characteristically broad features from 620 to 670 nm in the visible region and at 1072/1380 nm in the near-infrared region. From a comparison with previous investigations, we assign the spectroscopic fingerprints in the visible and the near-infrared to the one-electron oxidized form of the electron donating ZnP and the one-electron reduced form of the electron accepting C_{60}/C_{70}, respectively (Figures S68, S70, S72, and S74, Supporting Information). On longer time scales, the ZnP triplet excited state features dominate the transient absorption spectra with coexcited C_{60}/C_{70} excited-state transients. In accordance with these observations, global-target analyses of the raw data were run with a kinetic model (Figure 1) that involved coexcitations of, for example, complexed C_{60}²o and noncomplexed C_{60} and/or 2o. Similar fittings were performed for C_{60}⁶, C_{70}²o, and C_{70}⁶.

In the cases of C_{60}²o and C_{70}²o, four species models were applied to obtain reasonable convergence (Figures 11 and 13; Figures S69 and S71, Supporting Information). Two of them, that is, the first and second species, exhibit similar features with lifetimes on order of tens and hundreds of picoseconds, respectively. The features include those of the one-electron oxidized form of ZnP and the one-electron reduced form of C_{60}/C_{70}. The short lifetime of the first species, which is in the range from 4 to 15 ps, accounts for vibrational and structural relaxations to produce the energetically stabilized charge-separated state. As it is solvent polarity dependent (Table S8, Supporting Information) we attribute it to a charge-transfer state, that is, $C_{60}^{\bullet-}$@2o$^{\bullet+}$ and $C_{70}^{\bullet-}$@2o$^{\bullet+}$, and the second species to a charge-separated state, that is, $C_{60}^{\bullet-}$@2o$^{\bullet+}$ and $C_{70}^{\bullet-}$@2o$^{\bullet+}$. In toluene, the latter is subject to a ground-state recovery by means of charge recombination with lifetimes of 294 and 186 ps for $C_{60}^{\bullet-}$@2o$^{\bullet+}$/C_{70}^{\bullet-}@2o$^{\bullet+}$, respectively. In benzonitrile, the stabilization of the charge-separated state leads to lifetimes of 770 ps for $C_{60}^{\bullet-}$@2o$^{\bullet+}$/C_{70}^{\bullet-}@2o$^{\bullet+}$, respectively. In benzonitrile, the stabilization of the charge-separated state leads to lifetimes of 770 ps for $C_{60}^{\bullet-}$@2o$^{\bullet+}$/C_{70}^{\bullet-}@2o$^{\bullet+}$, respectively. In benzonitrile, the stabilization of the charge-separated state leads to lifetimes of 770 ps for $C_{60}^{\bullet-}$@2o$^{\bullet+}$/C_{70}^{\bullet-}@2o$^{\bullet+}$, respectively.
as the superimposed singlet excited state features of C70 and 2o. Notable is the fact that the excited state features stemming from the second singlet excited state of ZnP in uncomplexed 2o are unresolvable due to a fast internal conversion, on one hand, as well as the growth and subsequent decay of the charge-transfer and charge-separated state, on the other hand. In the following, the weakly populated triplet excited state as the fourth species persists on longer time scales and consists of transient characteristics stemming from C70 in the near-infrared region, that is, around 970 nm, and from 2o in the visible region, that is, in the range from 470 to 510 nm.\(^\text{[55]}\) When turning to C60@2o, contribution from the singlet and triplet excited states of uncomplexed 2o dominates the features of the third and fourth species, respectively. By virtue of its extremely low absorption cross-section at 430 nm, uncomplexed C60 is not seen.

In contrast, a three species model was sufficient to fit the data for C60@6 and C70@6 (Figures 12 and 13). Here, the second species is the charge-separated state, which is formed on an ultrafast timescale (<200 fs), and, which undergoes ground state recovery in benzonitrile with time constants of 130.7 ps for C60\(^{-}\)@6\(^{+}\) and 55.7 ps for C70\(^{-}\)@6\(^{+}\). In less-polar toluene, the charge-separated state is longer lived with 219 ps for C60\(^{-}\)@6\(^{+}\) and 162 ps for C70\(^{-}\)@6\(^{+}\). The initial formation of a charge transfer state, which eventually relaxes to afford the charge separated state, is only observed for C60@6 in toluene. One of the key advantages of templating three pairs of ZnPs accounts for the strong complexation of C60 and C70 via six complexation sites in 6 rather than one pair of ZnPs, which provides only a single complexation site in 2o, is supported by the observed stronger complexation of C60@6 and C70@6. Moreover, the stronger binding of C70 versus C60 is reflected in the excited state dynamics by the lack of transients assigned to uncomplexed 6 in C70@6 relative to C60@6 (Table S9 and Figures S73 and S75, Supporting Information).

4.3. Gas-Phase Inter(Porphyrin–Fullerene) Forces

Our investigations were rounded off by mass spectrometry-based gas-phase experiments. For example, electrospray ionization (ESI) of free-base porphyrin 6 (6H\(_4\)) by means of a quadrupole time-of-flight hybrid mass spectrometer leads to...
multiple protonations with up to four protons (Figure S77, Supporting Information). Additionally, clusters of $6\text{H}_2$ in varying charge states are detected.

When $C_{60}$ was present, the MS results provide evidence for an unprecedented complexation between $6\text{H}_2$ and $C_{60}$.[5,12] Signals corresponding up to nine $C_{60}$s are discernible in the mass spectra, for which an example is depicted in Figure 14. In other words, $6\text{H}_2$ acts as a sort of “$C_{60}$ sponge.” As in the case of just $6\text{H}_2$, multiple protonations are discernable (Figure S78, Supporting Information). Also, series of doubly and triply charged $C_{60}^{@6\text{H}_2}$ are abundantly detected. A slight signal intensity decrease is seen with increasing number of $C_{60}$s all the way of up to $(C_{60})_{8}^{@6\text{H}_2}$. Then, a significant intensity drop in, for example, $(C_{60})_{9}^{@6\text{H}_2}$ indicates a less favorable binding. The observed distribution is in line with a structure, in which six $C_{60}$s occupy the cavities between $H_2$Ps. Moreover, it should be reasoned that two additional $C_{60}$s bind to either side of the HBC core. Altogether, the HBC core and the tert-butyl groups of the $H_2$Ps are likely to form two additional “$C_{60}$ pockets.” Going beyond $(C_{60})_{8}^{@6\text{H}_2}$, that is, $(C_{60})_{9}^{@6\text{H}_2}$ etc. only weak van der Waals forces are operative.

Additionally, the fragmentation pattern was investigated by collision-induced dissociation (CID) experiments. Due to their similar mass-to-charge ratios, the triply charged $(C_{60})_{4}^{@6\text{H}_2}$ and the quadruply charged $(C_{60})_{8}^{@6\text{H}_2}$ were simultaneously mass selected and fragmented. In Figure 14b, the resulting MS/MS spectra at low and elevated collision energies are depicted. For $(C_{60})_{4}^{@6\text{H}_2}$ and $(C_{60})_{8}^{@6\text{H}_2}$, the consecutive loss of $C_{60}$s is detected in the fragmentation spectra. Ultimately, this resulted in $6\text{H}_2$ with three and four protons, respectively. For $(C_{60})_{8}^{@6\text{H}_2}$, the intermediate fragment ions are due to the loss of up to four $C_{60}$s pronounced in the low-energy CID spectrum, while those intermediate fragment ions, which are caused by the loss of all eight $C_{60}$s, are more pronounced in the CID spectrum recorded at moderate collision energies. The dissociation experiments provide further evidence for the presence of multiple $C_{60}$s and that the complexes with eight $C_{60}$s also exist with a higher charge-state than observed in the MS$^1$ spectrum.

To estimate the binding strength of the cavity by two porphyrins in ortho-position, energy dependent CID experiments were conducted with free-base porphyrin $2o$ ($2o\text{H}_2$).[5,12,56–58] A solution containing $2o\text{H}_2$ and $C_{60}$ was investigated by ESI-MS. The mass spectrum reveals the presence of the doubly protonated $2o\text{H}_2$ and the corresponding doubly protonated $C_{60}^{@2o\text{H}_2}$. The MS/MS experiment displays the dissociation of the complex into doubly protonated $2o\text{H}_2$ and neutral $C_{60}$. The $C_{60}^{@2o\text{H}_2}$ doubly protonated ion is further investigated by energy dependent CID. In these experiments, MS/MS spectra of $C_{60}^{@2o\text{H}_2}$ are recorded, while successively increasing the collision energy. From the MS/MS spectra the survival yield

![Figure 14. ESI mass spectrum (top) of $(C_{60})_{x}^{@6\text{H}_2}$ displaying signals assigned to complexes with up to $(C_{60})_{9}^{@6\text{H}_2}$. MS/MS fragmentation spectra (center) at lower and more elevated collision energies $E_{col}$. The spectra display the consecutive loss of $C_{60}$s from a triply and quadruply protonated $6\text{H}_2$ binding four and eight $C_{60}$s, respectively.](image-url)
(SY) of the mass-selected ion is plotted against the center-of-mass collision energy ($E_{\text{com}}$). The resulting plot resembles a sigmoidal curve (Figure 15) and $E_{\text{com}}$ at a survival yield of 0.5 ($E_{\text{com}}$/50) is used as a measure for the relative binding energy. To this end, a relative binding energy between $20\text{H}_2$ and $C_{60}$ of 0.72 eV is obtained. Performing experiments with $C_{60}@20\text{H}_2$ and $2\text{H}_2$ resulted in significantly lower binding energies for $C_{60}$, namely 0.33 eV. Thus, $C_{60}$ binds significantly stronger to $20\text{H}_2$ due to the tweezer-like binding motif.[59]

DFT geometry optimizations were performed for $20\text{H}_2$ and $2\text{mH}_2$ to investigate the differences between a monoporphyrin binding in $2\text{mH}_2$ and a diporphyrin binding in $20\text{H}_2$. $C_{60}$ was attached to the cavity formed by free-base porphyrin and the tert-butyl groups of the HBC–porphyrin conjugates.

$C_{60}@20\text{H}_2$ and $C_{60}@2\text{mH}_2$ were calculated as neutral and dicationic molecules with two additional protons at the porphyrins. Formation energies were calculated either as the energy difference between the optimized $C_{60}@20\text{H}_2/C_{60}@2\text{mH}_2$ and the sum of the optimized individual fullerene and the optimized individual $20\text{H}_2/2\text{mH}_2$ (further denoted as “optimized”), or as the energy difference between the optimized $C_{60}@20\text{H}_2/C_{60}@2\text{mH}_2$ and the sum of the optimized individual fullerene and $20\text{H}_2/2\text{mH}_2$ in the same geometry as in the complex (further denoted as “nonoptimized”). The individual molecules in the same geometry as in the complex should be considered as a formal intermediate in the formation and fragmentation of $C_{60}@20\text{H}_2/C_{60}@2\text{mH}_2$ (Figure 16).

The negative “nonoptimized” formation energy represent upper limits for the fragmentation energy as it describes a rapid fullerene loss without any immediate adaptation of the H$_2$P geometry. A faster adaptation of the geometry would lead to a lower fragmentation energy due to increasing interactions between the H$_2$Ps.

In $C_{60}@20\text{H}_2$, $C_{60}$ is encapsulated by both H$_2$Ps and interacts with both of them and their respective tert-butyl groups (Figure S79, Supporting Information). The magnitude of the “optimized” formation energy is lower compared to the “nonoptimized” formation energy because of stacking interactions in the optimized individual $20\text{H}_2$. This energy difference should be considered as an upper limit for the activation energy barrier for the formation of $C_{60}@20\text{H}_2$ (Figure 16). As the magnitude of “nonoptimized” formation energy of dicationic $C_{60}@20\text{H}_2$ is increased compared to neutral $C_{60}@20\text{H}_2$, the former ones are slightly more stable.

5. Conclusion

We investigated a full-fledged family of HBC–porphyrin conjugates with a broad arsenal of spectroscopic, crystallographic, and theoretical methods. Per se, HBC offers unique possibilities for realizing different substitution patterns, namely ortho, meta, and para, which are normally found in phenyl rings. All of the aforementioned offered unique incentives to probe (inter)porphyrin and (inter)porphyrin–fullerene interactions in the absence and presence of $C_{60}$ and $C_{70}$, respectively.

It is within the context of (inter)porphyrin interactions of great value that electron-vibration couplings between individual porphyrins across the HBC platform as a function of substitution pattern were corroborated by Soret-band splits in the
steady-state absorption measurements and by delocalization of the ZnP singlet excited states and/or rotational relaxations between the porphyrins in transient absorption experiments. Considering that the strongest interactions were seen in the para-isomer and the weakest in the ortho-isomer underline the importance of the geometrical arrangement for the study of distinct photophysical properties. TDDFT calculations on the natural transition orbitals of the high- and low-energy Soret-band splits highlighted their localized and delocalized nature, respectively, and documented exemplarily that interporphyrinyl communication across the HBC platform is operative.

With respect to (inter)porphyrin–fullerene interactions, electron donor–acceptor experiments with $C_{60}$ and $C_{70}$ were feasible due to the unique architecture of the HBC–porphyrin conjugates. Titration experiments revealed strong ground- and excited-state interactions, resulting in binding constants as large as $8.7 \times 10^6$ M$^{-1}$. Generally speaking, binding of $C_{70}$ was stronger than binding of $C_{60}$. In transient absorption experiments, fast and efficient charge separation followed by charge recombination afforded the ground and triplet excited states. The good fit of $C_{60}$ and $C_{70}$ with the porphyrin cavity was also investigated in the gas phase by mass spectrometry measurements, which emphasize the high stability. This led to a maximal binding of up to nine $C_{60}$.s. Complementary DFT calculations showed exemplarily how important the formation of a diphosphoryncavity is for binding $C_{60}$ and $C_{70}$. Next to liquid and gas phase experiments, solid-state measurements with cocrystals of $C_{60}$ and the HBC–porphyrin conjugates were presented. By means of X-ray diffraction, the cocrystals were closer analyzed. The cocrystals documented the compatibility of the diphosphoryncavity of the ortho-isomer with $C_{60}$ and the formation of 1D wires of the para-isomer with $C_{60}$.

6. Experimental Section

**Steady-State and Time-Resolved Photophysical Measurements:** All chemicals were purchased from Sigma-Aldrich and used without any further purification. A Perkin Elmer Lambda 2 spectrometer was used in order to collect the UV–vis spectra at 298 K using a scan rate of 480 nm min$^{-1}$. The data were recorded with the help of UV WinLab software. Steady-state fluorescence studies were conducted using Fluoromax 3 spectrometer (Horiba Scientific). Time-resolved absorption studies were performed by using the Clark MXR CPA 2101 and CPA2110 Ti:sapphire amplifier (775 nm, 1 kHz, 150 fs pulse width) as the laser source. Ultrafast Systems HELIOS femtosecond transient absorption spectrometer was used to acquire time resolved transient absorption spectra with 150 fs resolution and time delays from 0 to 5500 ps. The probe-visible white light ($\approx$400–770 nm) was generated by focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk. And, for the (near) IR (780–1500 nm), a 1 cm sapphire was used. Noncollinear optical parameter (NOPA, Clark MXR) was used to generate the excitation wavelength at 430 nm; a bandpass filter ±5 nm was used to exclude the fundamental 775 and 387 nm. The excitation at 387 nm was tuned by frequency doubling using a calcium fluoride nonlinear optical crystal. All measurements were performed in 1 cm quartz cuvettes under argon atmosphere. The data points in the 450–470 and 765–790 nm regimes were removed as they stem from the pump excitation and fundamental excitation wavelength, respectively. In order to deconvolute associated species, the spectral data were subjected to global-target analysis, which is based on an excited-state deactivation kinetic model. To carry out the analysis, the free software program GloTarAn was used, which is a graphical interface to the R-package TIMP. Origin 2018/2019/2020-pro version was used to plot the data obtained using different spectroscopic and analytical methods. Time correlated single-photon counting (TCSPC) experiments were recorded with a FluoroLog-3 lifetime spectrophotofluorometer from Horiba Jobin Yvon with integrated TCSPC software. The samples were excited at 400 nm by a SuperK Extreme EXB-6 laser from NKT Photonics.

**Mass Spectrometry:** ESI mass spectra were recorded either with a micrOTOF-Q II or a maXis (both Bruker, Germany) both quadrupole time-of-flight hybrid mass spectrometers each equipped with an electrospray ion-source using nitrogen as nebulizing gas and a collision quadrupole also utilizing nitrogen as collision gas. Parameter settings were adjusted to obtain maximum signal intensity.

Collision-induced dissociation experiments were conducted by mass selecting ions and subsequently accelerating them through a nitrogen filled collision quadrupole. Energy dependent fragmentation experiments can be conducted by varying the acceleration potential ($E_{\text{acc}}$) and plotting the survival yield (SY) of the precursor ion against the collision energy in the center of mass range ($E_{\text{com}}$). SY and $E_{\text{com}}$ are given by Equations (1) and (2), respectively

$$\text{SY} = \sum \text{Int(Prec)} / (\sum \text{Int(Prec)} + \sum \text{Int(Frag)})$$

(1)

$$E_{\text{com}} = m(N_{f}) \times E_{\text{acc}} / (m(N_{f}) + m(\text{Prec}))$$

(2)

The data points are then fitted with a sigmoidal Boltzmann fit

$$f(x) = \frac{A_1 - A_2}{1 + e^{-\frac{x-x_0}{d_0}}} + A_2$$

(3)

$A_1$ and $A_2$ are the beginning and ending value, respectively, and $d_0$ refers to the width of the steepest part of the sigmoid curve. The inflection point is given by $x_0$. As a measure for the binding energy, the $E_{\text{com}}$ is taken at the position at which the SY = 0.5($E_{\text{com}}+E_{\text{com}}$).

Spraying solutions for the samples containing fullerenes were prepared in a DCM:methanol:toluene (1:1:1, v/v/v) mixture. The respective HBC–porphyrin concentration was adjusted to $5 \times 10^{-6}$ mol L$^{-1}$, whereas the fullerene concentration had a two- to tenfold excess. The spraying solutions to investigate solely an HBC–porphyrin was prepared in a DCM:methanol (1:2, v/v) mixture with a concentration of the anlyte of $5 \times 10^{-6}$ mol L$^{-1}$. In both scenarios TFA was added to enable protonation of the HBC–porphyrin.

**Computational Details on Soret-Band Splitting Calculations:** The density-functional theory calculations (DFT) were performed using the Turbomole program package Version 6.6 and 7.3. Different orientations of the porphyrins and the phenyl groups of free-base 2o, 2m, 2p, and 1 without tert-butyl groups have been optimized using the PBE[62] functional and the def2-TZVP[63] basis set. The most stable conformation was reoptimized using the B3-LYP[64,65] functional after replacement of the two protons with zinc to obtain 2o, 2m, and 2p (see SI for details). The spectra were then calculated using the BHLYP[66] functional and the def2-SVP[63] basis set (see SI for comparison between free-base 2p with the def2-SVP basis set and the def2-TZVP basis set). For 2o, the most important tert-butyl groups were added for the geometry-optimization and removed for the calculation of the spectra (see SI for details). Solvent effects were taken into account using the conductor-like screening model (COSMO)[67] method. For the free base porphyrins, the dielectric constant and refractive index of THF ($\epsilon = 7.52; n = 1.405$)[68] was used, while the dielectric constant and refractive index of toluene ($\epsilon = 2.379; n = 1.4941$)[68] was used in case of the zinc porphyrins. For all calculations, dispersion interactions were included via the semiempirical D3 dispersion interaction correction developed by Grimme et al., including Becke–Johnson damping.[69,70]

Visual Molecular Dynamics software (VMD) (versions 1.9.3 and 1.9) was used to plot the NT0s.[71]
**Computational Details**

The TURBOMOLE software package (Version 7.2) was used to perform all density-functional calculations. PBE[62] was chosen on the triple-zeta basis set def2-TZVP[63] Dispersion interactions were taken into account by employing the Grimme D3 dispersion correction.[69]

In order to visualize intermolecular van der Waals (VdW) interactions the program NCIPLOT (Version 3.0)[73] was used to calculate contour plots of the reduced density gradient (RDG)

\[
\text{RDG} = \frac{-1}{2(3\pi)^{1/2}} \frac{\nabla^2 \rho}{\rho^{3/2}}
\]

which were visualized at low electron density \(\rho\), i.e., electron densities below a certain threshold. Here, a threshold value of \(\rho = 0.2\) was chosen for the electron density.

The second largest eigenvalue of the electron density Hessian matrix \(\lambda_{2}\) was used in the expression \(\text{sign}(\lambda_{2})\rho\) to identify attractive long-range interactions between fullerene and porphyrin. The RDGs indicating noncovalent interactions are displayed at isosurfaces of 0.3 au. The color dispersion correction.

The large majority of the literature uses the program NCIPLOT (Version 3.0)[73] to visualize intermolecular VdW interactions.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or on request to privacy or ethical restrictions.

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

**Keywords**

charge separation, crystal structure, fullerene, hexaazocoronene, porphyrin, transient absorption

Received: January 15, 2021
Revised: February 6, 2021
Published online: March 11, 2021

[1] A. Zieleniewska, F. Lodermer, A. Roth, D. M. Guldi, Chem. Soc. Rev. 2018, 47, 702.
[2] A. Lembo, P. Tagliasta, D. M. Guldi, J. Phys. Chem. A 2006, 110, 11424.
[3] X. Yu, B. Wang, Y. Kim, J. Park, S. Ghosh, B. Dhara, R. D. Mukhopadhyay, J. Koo, I. Kim, S. Kim, I.-C. Hwang, S. Seki, D. M. Guldi, M.-H. Baik, K. Kim, J. Am. Chem. Soc. 2020, 142, 12596.
[4] A. Lembo, P. Tagliasta, D. M. Guldi, M. Wielopolski, M. Nuccetelli, J. Phys. Chem. A 2009, 113, 1779.
[5] S. Jung, J. D. van Pauwede, P. D. W. Boyd, S. K. Shin, Phys. Chem. Chem. Phys. 2011, 13, 20248.
[6] V. Nikolaou, A. Charisiadis, C. Stangel, G. Charalambidis, A. G. Coutssoleos, C. J. Carbon Res. 2019, 5, 57.
[7] R. Kaur, S. Sen, M. C. Larsen, L. Tavares, J. Kjelstrup-Hansen, M. Ishida, A. Zieleniewska, V. M. Lynch, S. Bähring, D. M. Guldi, J. L. Sessler, A. Jana, J. Am. Chem. Soc. 2020, 142, 11497.
[8] G. Yzambart, A. Zieleniewska, S. Bauroth, T. Clark, M. R. Bryce, D. M. Guldi, J. Phys. Chem. C 2017, 121, 13557.
[9] R. Kaur, F. Possanzen, F. Limosani, S. Bauroth, R. Zanoni, T. Clark, G. Arrigoni, P. Tagliasta, D. M. Guldi, J. Am. Chem. Soc. 2020, 142, 7898.
[10] Y. Sun, T. Drovettskaya, R. D. Bolskar, R. Bau, P. D. W. Boyd, C. A. Reed, J. Org. Chem. 1997, 62, 3642.
[11] P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, S. F. Tham, C. A. Reed, J. Am. Chem. Soc. 1999, 121, 10487.
[12] S. Jung, J. Seo, S. K. Shin, J. Phys. Chem. A 2010, 114, 11376.
[13] P. Bhryappa, K. Karunanithi, Inorg. Chem. 2010, 49, 8389.
[14] Y. Xu, B. Wang, R. Kaur, M. B. Minameyer, M. Bothe, T. Drewello, D. M. Guldi, M. von Delius, Angew. Chem., Int. Ed. 2018, 57, 11549.
[15] B. Wang, S. Bauroth, A. Saha, M. Chen, T. Clark, X. Lu, D. M. Guldi, Nanoscale 2019, 11, 10782.
[16] D. Sun, F. S. Tham, C. A. Reed, L. Chaker, P. D. W. Boyd, J. Am. Chem. Soc. 2002, 124, 6604.
[17] K. Tashiro, T. Aida, J. Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto, K. Yamaguchi, J. Am. Chem. Soc. 1999, 121, 9477.
[18] Y. Shiyo, K. Tashiro, T. Aida, J. Am. Chem. Soc. 2004, 126, 6570.
[19] D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess, P. D. W. Boyd, J. Am. Chem. Soc. 2000, 122, 10704.
[20] L. Chen, Y. Hernandez, X. Feng, K. Mullén, Angew. Chem., Int. Ed. 2012, 51, 7640.
[21] A. Narita, X.-Y. Wang, X. Feng, K. Müllen, Chem. Soc. Rev. 2015, 44, 6636.
[22] R. Rieger, K. Müllen, J. Phys. Org. Chem. 2010, 23, 315.
[23] D. Reger, P. Haines, F. W. Heinemann, D. M. Guldi, N. Jux, Angew. Chem., Int. Ed. 2018, 57, 5938.
[24] J. Holzwarth, K. Y. Amsharov, D. I. Sharapa, D. Reger, K. Roshchyna, D. Lungerich, N. Jux, F. Hauke, T. Clark, A. Hirsch, Angew. Chem., Int. Ed. 2017, 56, 12184.
[25] J. M. Englert, J. Malig, V. A. Zamolo, A. Hirsch, N. Jux, Chem. Commun. 2013, 49, 4827.
[26] D. Lungerich, J. F. Hitzenberger, M. Marcia, F. Hampel, T. Drewello, N. Jux, Angew. Chem., Int. Ed. 2014, 53, 12231.
[27] D. Lungerich, J. F. Hitzenberger, W. Donaubauer, T. Drewello, N. Jux, Eur. J. Chem. 2016, 22, 16735.
[28] D. Lungerich, J. F. Hitzenberger, F. Hampel, T. Drewello, N. Jux, Chem. – Eur. J. 2018, 24, 15383.
[29] M. M. Martin, D. Lungerich, P. Haines, F. Hampel, N. Jux, Angew. Chem., Int. Ed. 2019, 58, 8932.
[30] M. M. Martin, D. Lungerich, F. Hampel, J. Langer, T. K. Ronson, N. Jux, Eur. J. Chem. 2019, 25, 15083.
[31] M. Wolf, D. Lungerich, S. Bauroth, M. Popp, B. Platter, T. Clark, H. L. Anderson, N. Jux, D. M. Guldi, Chem. Sci. 2020, 11, 7123.
[32] M. Ruppel, L.-P. Gazetas, D. Lungerich, N. Jux, Eur. J. Org. Chem. 2020, 2020, 6352.
Intriguingly, the ratio of the Q-band absorptions, namely (1–*0)-versus (0–*0)-transitions, changes when compared with respect to the ZnTPP reference. In toluene, the corresponding ratios range from 0.27 to 0.30, while that for ZnTPP is 0.18. Even higher are the ratios in benzonitrile: 0.53 to 0.58 (Figures S2 and S3). The Q-band extinction coefficients of 1 as well as of 2o, 2m, and 2p are equal and doubled, respectively, relative to ZnTPP. 6, in contrast, diverts from this correlation with extinction coefficients that are only marginally higher than those found in 2o, 2m, and 2p.

R. L. Martin, J. Chem. Phys. 2003, 118, 4775.

A qualitative discussion and the corresponding data and images are shown in the S1—pages S5–S 41.

Compared to the ZnTPP reference, the higher quantum yields of the HBC–porphyrin conjugates stem from the energy transfer between photoexcited HBC and ZnP.

Fluorescence lifetimes, determined in time-correlated single photon counting (TCSPC) experiments by recording the 645 nm fluorescence wavelength after photoexciting at 430 nm into the Soret-band absorption spectra of the individual components. Fluorescence lifetimes are similar to those determined for the ZnTPP reference (Figure S40 and Table S4).

J. A. G. Williams, J. T. Hupp, J. Am. Chem. Soc. 2011, 133, 12772.

The co-excited uncomplexed ZnTPP and C 60, or C 70, which, relative to the complexed C 60@ZnTPP or C 70@ZnTPP share very low population magnitude, exhibit intrinsic excited-state dynamics.

The attribution or explanation for the third and fourth species spectral features were based on the comparison with the transient absorption spectra of the individual components.

J. F. Hitzenberger, P. O. Dral, U. Meinhardt, T. Clark, W. Thiel, M. Kivala, T. Drewello, ChemPlusChem 2017, 82, 204.

R. W. Kirschbaum, M. Haussmann, O. V. Boltalina, S. H. Strauss, T. Drewello, Phys. Chem. Chem. Phys. 2015, 17, 23052.

J. Li, K. Duerr, M. S. von Gernler, N. Jux, I. Ivanović-Burmazović, T. Drewello, Int. J. Mass Spectrom. 2013, 354-355, 406.

The relative binding energies of free-base 2m (2mH2) and free-base 2p (2pH2) are only just exceeding the one of the singly protonated complex consisting of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (otBuTPPP) and C 60 which serves as a reference in Figure 15.

Turbomole V6.6 2014 and V7.3 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989, Turbomole GmbH, since 2007.

R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 1989, 162, 165.

J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.

J. F. Hitzenberger, P. O. Dral, U. Meinhardt, T. Clark, W. Thiel, M. Kivala, T. Drewello, ChemPlusChem 2017, 82, 204.

R. W. Kirschbaum, M. Haussmann, O. V. Boltalina, S. H. Strauss, T. Drewello, Phys. Chem. Chem. Phys. 2015, 17, 23052.

J. A. G. Williams, J. T. Hupp, J. Am. Chem. Soc. 2011, 133, 12772.

The relative binding energies of free-base 2m (2mH2) and free-base 2p (2pH2) are only just exceeding the one of the singly protonated complex consisting of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin (otBuTPPP) and C 60 which serves as a reference in Figure 15.

Turbomole V6.6 2014 and V7.3 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989, Turbomole GmbH, since 2007.

R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 1989, 162, 165.

A. Zienleniewska, S. R. Harper, D. P. Arnold, D. M. Guldi, Chem. – Eur. J. 2018, 24, 3058.

TDDFT calculations of the high- and low-energy Soret-bands are in sound agreement with the delocalization of the ZnP singlet excited state as visualized by the repopulation of the low-energy Soret-band bleaching in the TAS measurements.

C. E. Tait, P. Neuhaus, H. L. Anderson, C. R. Timmel, J. Am. Chem. Soc. 2015, 137, 6670.

C. She, J. E. McCarraah, S. J. Lee, J. L. Goodman, S. T. Nguyen, J. A. G. Williams, J. T. Hupp, J. Phys. Chem. A 2009, 113, 8182.