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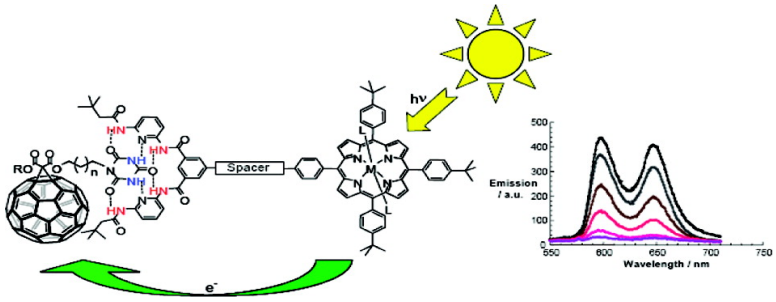

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Implementation of a Hamiliton-Receptor-Based Hydrogen-Bonding Motif toward a New Electron Donor−Acceptor Prototype: Electron versus Energy Transfer

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Abstract: A new modular concept for the self-assembly of electron donor−acceptor complexes is presented that ensures (i) fine-tuning the strength of the complexation, (ii) controlling the electronic coupling to impact electron and energy transfer processes, and (iii) high solubility of the corresponding hybrid architectures. This task has been realized through developing a series of porphyrin−fullerene donor−acceptor systems held together by a Hamilton-receptor-based hydrogen-bonding motif. In this context, novel libraries of C_{60} monoadducts (**1**) containing cyanuric acid side chains and of tetraphenylporphyrin derivatives (**2**) involving the complementary Hamilton-receptor unit were synthesized. The association constants of the corresponding 1:1 complexes (**1·2**) connected by six hydrogen bonds were determined complementary by NMR and fluorescence assays. Their strength, which was found to be in the range between 3.7×10^3 and 7.9×10^5 M^{-1}, depends on the nature of the spacers, namely, hexylene versus propylene chains. Finally, transient absorption studies revealed photoinduced electron transfer from ZnP to C_{60} in the corresponding **1·2** complexes, which generate radical ion pair states that are persistent well beyond the ns time scale. In the case of the analogous SnP complexes, energy instead of electron transfer was observed. This is due to the shift of oxidation potential caused by presence of Sn in the oxidation state of +4.

Introduction

The transport of energy and electrons within nanoscale-ordered materials is critical to the realization of systems for artificial photosynthesis as well as engineering molecular electronics and optoelectronics.[1] Studying multifunctional fullerene nanostructures—their design, synthesis, characterization, and performance—mandates a careful control over composition, interchromophore separation/angular relationship, overall dynamical and stimulus-induced reorganization, and electronic coupling. The overall goal is to achieve control over both the organization of the assemblies and their physical and chemical properties (i.e., electronic structures, etc.) and, thereby, enhance desired functionalities, through simple external parameters or variables, with the intent of creating new tailored materials. Among the tools exploitable for the creation of new assemblies are organization principles, such as biomimetic methodologies, that help regulate size, shape, and function down to the molecular scale.[2] Nature has long used these interactions to create a formidable array of structures, where a great level of control over the organization and an increased flexibility in replacing individual building blocks have been realized.

Nanohybrid systems that combine the favorable features of, for example, fullerenes and porphyrins as electron acceptors and electron donors, respectively, have received considerably interest.[3] As a consequence, new materials with a wide range of unique and spectacular physicochemical properties have resulted in noteworthy advances in the areas of light-induced electron-transfer chemistry and solar energy conversion. It is mainly the small reorganization energy, which fullerenes exhibit in electron-transfer reactions, that is accountable for a noteworthy breakthrough.[4] In particular, ultrafast charge separation together with very slow charge recombination features lead to unprecedented long-lived radical ion pair states formed in high quantum yields. This aspect is crucial toward the use of solar

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(1) For a recent status report, see: Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668.

(2) (a) McDermott, G.; Priece, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaaacs, N. W. *Nature* **1995**, *374*, 517−521. (b) Barber, J. *Nature* **1988**, *333*, 114−114. (c) Balzani, V., de Cola, L., Eds. *Supramololcular Chemistry*; NATO ASI Series; Kluwer Academic Publishers: Dordrech, The Netherlands, 1992. (d) Steed, J. W.; Atwood, J. *Supramol. Chem.* Wiley: Chichester, U.K., 2000. (e) Balzani, V.; Venturini, M.; Credi, A. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, Germany, 2003. (f) Ozin, G. A.; Arsenault, A. C. *Nanochemistry*; RSC Publishing: Cambridge, U.K., 2005.

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energy conversion as a clean, abundant, and economical energy source.

To this end, most electron donor−acceptor systems are based on covalently linking, at least, two building blocks. Important is that the bridges between the donor and acceptor govern the donor−acceptor distance, spatial orientation, and flexibility. Much less is, however, known about noncovalent fullerene electron donor−acceptor nanohybrids and the function of the intervening spacers.[5] In a recent example, which was built on noncovalent electrostatic interactions, where oppositely charged fullerenes and porphyrins/cytochrome *c* interact tightly with each other, sufficiently strong electronic couplings powered an intrahybrid charge separation.[6] This approach turned out to be especially successful for constructing photovoltaic devices that perform efficiently on the basis of photoinduced electron transfer between the hierarchically ordered building blocks.[7]

There is little, if any, doubt that the most potent supramolecular binding motif is, nevertheless, hydrogen bonding. Despite its tremendous potential for the realization of highly directional self-assembly, only a few examples of fullerene−porphyrin donor−acceptor nanohybrids have been constructed in this way so far.[8]

We have recently introduced the Hamilton-receptor[9a]/cyanuric acid binding motif to self-assemble new dendrimer prototypes (Figure 1).[9b−e] Importantly, the six-point hydrogen bonding leads to comparatively strong bindings between hosts and guests with

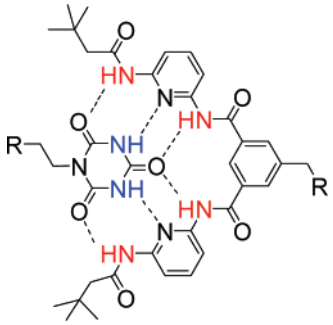

Figure 1. Schematic representation of the complementary hydrogen-bonding motif of a cyanuric acid derivative and a Hamilton receptor.

association constants $K_{ass.}$ that range in apolar solvents (i.e., dichloromethane and toluene) between 10^3 and 10^6 M^{-1}. Besides dendritic achiral and chiral building blocks such as depsipeptide dendrons, we have also tested chromophoric components to self-assemble into novel dendrimeric architectures, namely, fullerene-neated cyanuric acid end-caps and Hamilton-receptor substituted porphyrin cores. Important is that, in these architectures, the fullerene and porphyrin building blocks were integrated separately and just served as assembly determining building blocks or as sensors for chirality transfer.

A significant set back is the poor solubility of the Hamilton-receptor/cyanuric acid motif caused by inter- and intramolecular aggregation,[9] which is quite cumbersome for supramolecular complexation experiments. To overcome this deficiency, we have developed in the current work for the first time highly soluble supramolecular porphyrin/fullerene dyads. Thereby the association constants of these complexes could be determined even in apolar solvents like toluene.

The strategy toward hydrogen-bonded electron donor−acceptor nanohybrids developed in the current contribution is sketched in Figure 2. In particular, fullerene **1** is a monomalonate, where one branch carries a cyanuric acid moiety. The corresponding linkers are either propylene or hexylene chains. The second malonate branch, on the other hand, contains a variety of dendritic termini that assist in guaranteeing high solubility in solvents that do not compete with hydrogen bonding (i.e., chloroform and dichloromethane). At the end of the porphyrins (**2**), one of the four phenyl rings bears the Hamilton-receptor connected via an amide spacer. To add diversity we have pursued—besides free base porphyrin derivatives (i.e., H_2P)—the coordination of either tin or zinc as central metals. Whereas the Zn derivatives (i.e., ZnP) involve a tetragonal planar (NMR time scale) coordination motif, the Sn analogues (i.e., SnP) exhibit an octahedral coordination pattern with two additional axial ligands.

Results and Discussion

We have recently reported the syntheses of compounds **1e**,**f**, where a propylene spacer unit between the malonate and the cyanuric acid moiety ($n = 1$) was employed.[1c] To increase the

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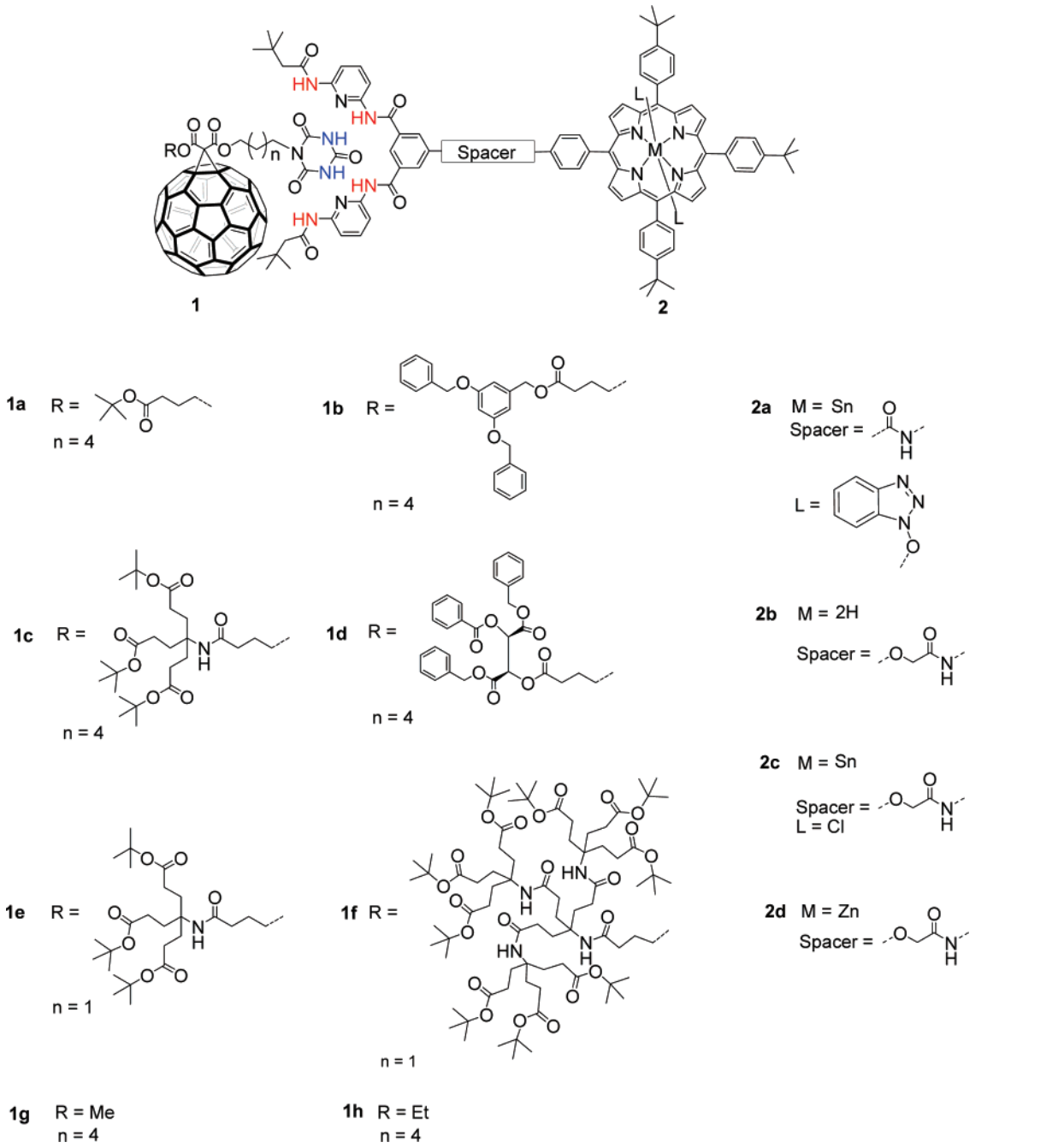

Figure 2. Schematic represention of the **1·2** complexes between fullerene cyanurates and porphyrin-Hamilton receptors associated by 6-fold hydrogen bonding.

flexibility and to facilitate the binding we introduce in this study the syntheses of hexylene analogues. These were prepared by following a modified synthetic procedure. For the syntheses of the fullerene cyanurates **1** suitable malonate precursors were prepared *prior* to the cyclopropanation of C_{60}[10] and subsequent linkage of the cyanuric acid moiety. The sequence started from 1-bromohexane-6-ol, which was coupled with the monoacid **3** using standard ester coupling conditions (Scheme 1). The resulting asymmetric malonate **4a** was then treated with trifluoroacetic acid (TFA) to provide acid **5**. The latter serves as anchor for the subsequent coupling of the corresponding dendritic termini. The bromomalonates **4b**−**d** were obtained by modified Steglich conditions[11] using dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBT), and diaminopyridine (DMAP) with yields up to 89% (Scheme 1).

For comparison we also synthesized the nondendric malonates **4e**,**f** by simple treatment of methyl and ethyl malonyl chloride with 1-bromohexane-6-ol (Scheme 2).

The fullerene monoadducts **6** were synthesized by standard Bingel[10] conditions (Scheme 3). In the case of chiral malonyl system **6c** and the malonates **6g**,**h** clean cyclopropanation was only successful by using iodine instead of CBr_4 for the activation of the central methylene group.

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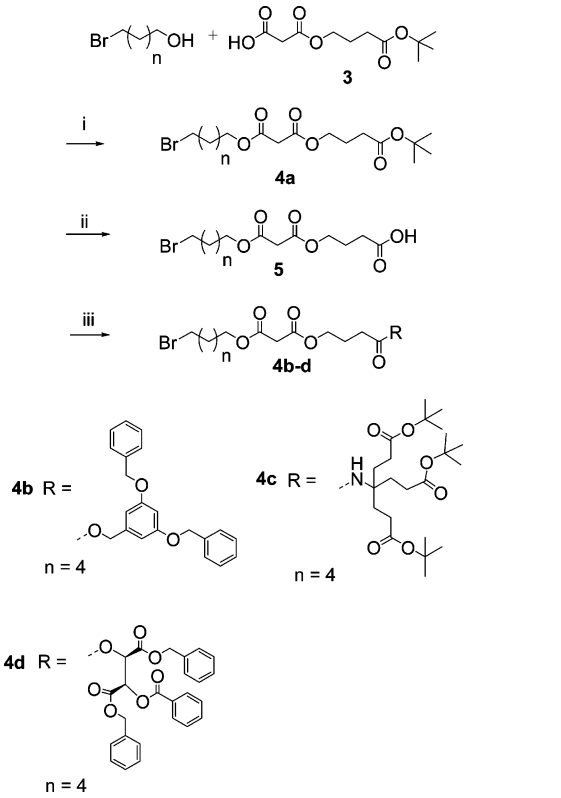
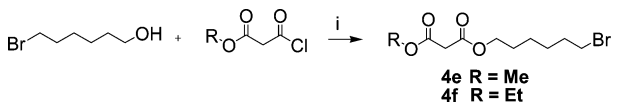
Scheme 1. Syntheses of the Dendromalonates **5a**−**d**[a]



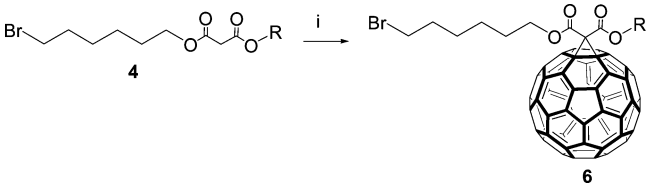
[a] Key: (i) DCC, HOBT, DMAP, CH_2Cl_2, 0 °C; (ii) TFA, CH_2Cl_2, RT; (iii) dendrimer, DCC, HOBT, DMAP, CH_2Cl_2, 0 °C.

Scheme 2. Syntheses of Malonates **4e**,**f**[a]



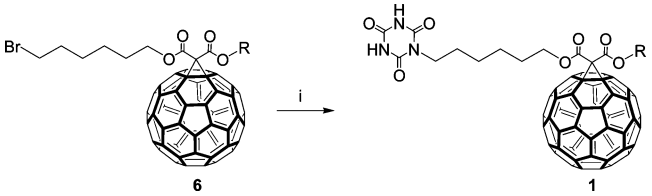
[a] Key: (i) pyridine, CH_2Cl_2, 0 °C.

Scheme 3. Syntheses of the C_{60} Monoadducts **6**[a]



[a] Key: (i) C60, I_2, CBr_4, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, RT.

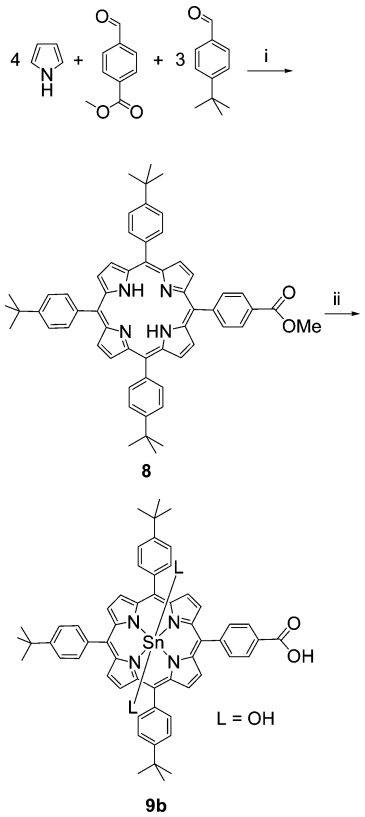
Scheme 4. Synthesis of the Fullerene−Cyanuric Acid Derivatives **1**[a]



[a] Key: (i) cyanuric acid, DBU, DMF, 40 °C.

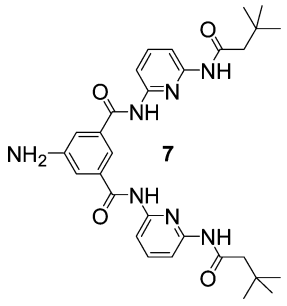
The final step in the synthesis of the target adducts **1** was a S_N2 substitution of the terminal bromine atom with cyanuric acid (Scheme 4). Here, cyanuric acid was first deprotonated with DBU to facilitate the substitution. The insertion of the cyanuric acid had to be performed in the last reaction step due to the low reactivity of the C_{60} monoadducts **6**.

Scheme 5. Synthesis of the Porphyrin Building Blocks **8** and **9b**[a]



[a] Key: (i) $BF_3{\cdot}OEt_2$, DDQ, CH_2Cl_2, RT; (ii) (1) $SnCl_2$, acetic acid, (2) NaOH, ethanol, reflux.

For the synthesis of the Hamilton-receptor-substituted porphyrin **2a** involving a very rigid spacer unit, amino derivative **7**[12] was used as building block for the coupling with a suitable tetraphenylporphyrin (TPP) derivative. For this purpose the metal free methyl ester **8** containing three peripherical *tert*-butyl substituents was chosen due to an increase in the overall solubility. Conceptually, this TPP derivative can subsequently be metalated and transformed into the free acid for further coupling reactions.



The synthesis of **8** was carried out by a typical Lindsey procedure[13] using a 4:1:3 mixture of pyrrole, methyl 4-formylbenzoate, and 4-*tert*-butylbenzaldehyde as precursors for the statistical condensation reaction (Scheme 5). Boron trifluoride

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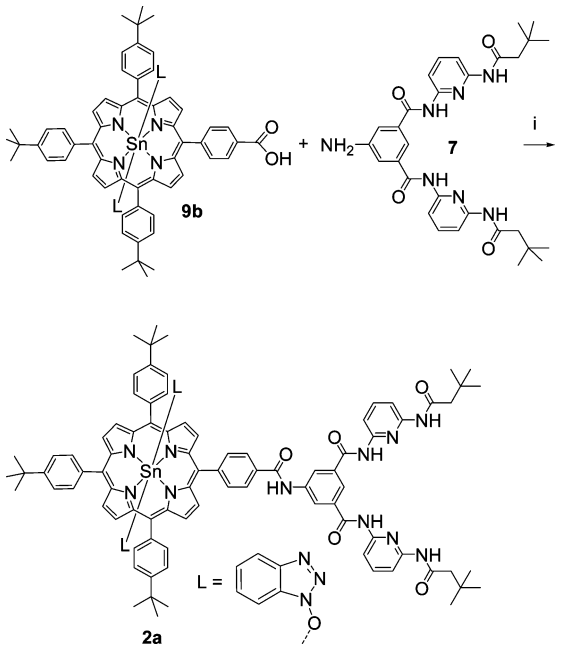
Scheme 6. Synthesis of the Hamilton-Receptor-Bearing Porphyrin **2a**[a]



[a] Key: (i) 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC), HOBT, DMAP, CH_2Cl_2, 0 °C.

diethyl etherate was used as catalyst to promote the cyclization reaction. For the final oxidation 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used as oxidant. Due to the low solubility of the corresponding deprotected free carboxylic acid, we decided to metalate the porphyrin prior to the deprotection (Scheme 5).

Tin(II) chloride was used for the metalation of **8**, since when complexed by a porphyrin, the most stable oxidation state of +4 binds typically two anionic axial ligands. In such architectures direct $\pi-\pi$-contacts between the fullerene and porphyrin chromophores should not prevail. As a consequence electronic interactions can only be accomplished through bonds involving the H-bonding motif represented in Figure 1. After evaluation of the literature precedents describing methods for the insertion of tin into free base porphyrins,[14] we decided to use the acetic acid method, because the insertion is nearly quantitative and the solvent can easily be removed by rotary evaporation. In this regard, free base porphyrin **8** was dissolved in acetic acid in the presence of $SnCl_2$ and heated under reflux. During the reaction Sn(II) was oxidized from the oxidation state of +2 to +4. At the same time two chloride ligands bind in axial positions. The subsequent deprotection was achieved by treatment with NaOH. During this procedure the axial chloride ligands were replaced by hydroxide to give the desired compound **9b**, which is sufficiently soluble in apolar solvents. The protons of the hydroxo ligands appear as a broad singlet at −7.5 ppm in the ^{1}HNMR spectrum of **9b** recorded in $CDCl_3$. Since the protons of the hydroxo ligands are fairly acidic, we expected that at least a 3-fold excess of HOBT has to be used for the final Steglich coupling[9] with Hamilton-receptor **7** to obtain the target compound **2a** where both hydroxo ligands are replaced by two hydroxybenzotriazole molecules (Scheme 6).

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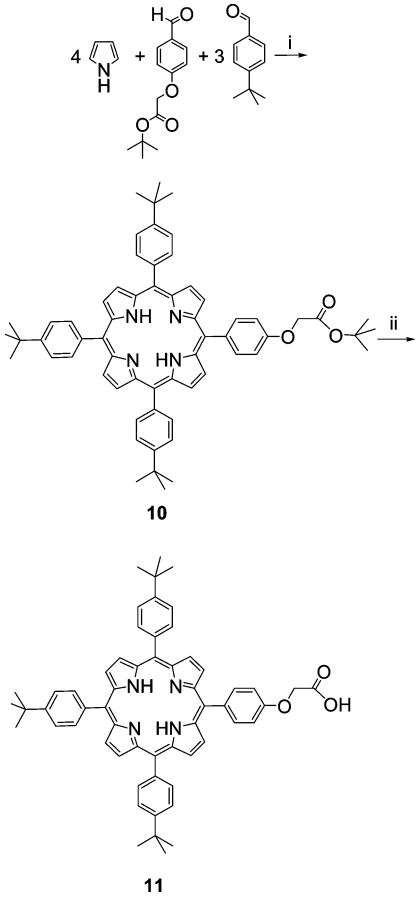
Scheme 7. Synthesis of the Porphyrin Derivative **11**[a]



[a] Key: (i) BF_3·OEt_2, DDQ, CH_2Cl_2, RT; (ii) formic acid, RT.

Indeed, no coupling was observed by using just 1 equiv of coupling reagents. However, when 3 equiv of the coupling reagent was used, the target compound **2a** was obtained as the major reaction product.

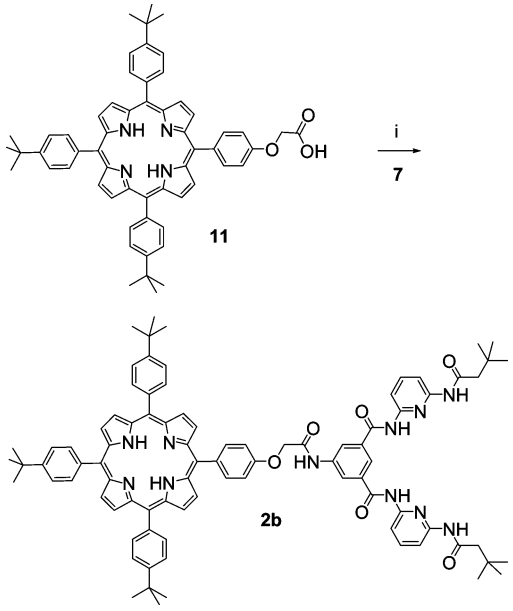
To introduce a more flexible spacer between the Hamilton receptor and porphyrin part of **2** (Figure 2)—for reasons of comparison—we decided to synthesize also the free base porphyrin precursor **10**. The synthesis of **10** was again carried out using modified Lindsey conditions (Scheme 7). The subsequent treatment of **10** with formic acid afforded porphyrin **11**, which is very soluble in apolar solvents. In this case metalation prior to the deprotection was not required.

Significantly, the subsequent coupling of **11** with the Hamilton receptor **7** (Scheme 8) proceeded in higher yield (30%) compared to that of **9b** with **7** (18%). This is due to the fact that the aliphatic carboxylate is more reactive than the aromatic carboxlate involved in **9b**.

The free base porphyrin **2b** served as a versatile precursor for the final metalation step. After treatment with $SnCl_2$ and $Zn(OAc)_2$ the metalloporphyrins **2c**,**d** were obtained in excellent yields (Scheme 9).

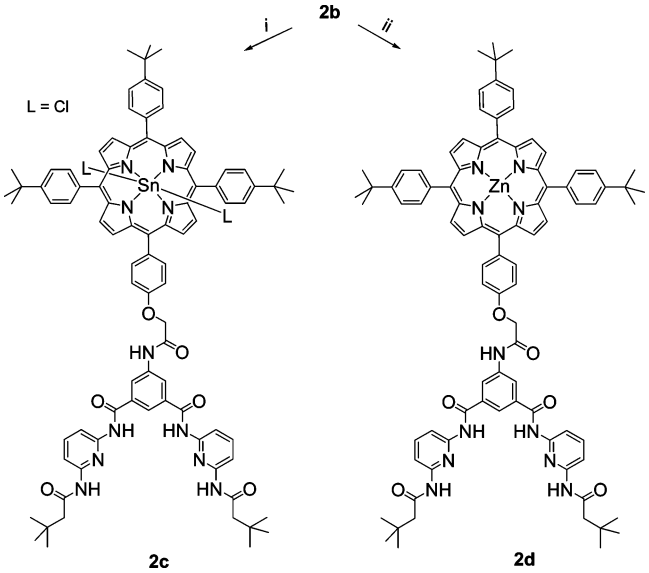
The formation of the **1**·**2** complexes was first investigated by ^{1}H NMR spectroscopy. In particular, the determination of the association constant $K_{ass.}$ required a series of titration experiments in $CDCl_3$. The characteristic downfield shifts of the NH^1- and NH^2-protons of the Hamilton-receptor moieties[9b−e] in **2a** were used to analyze the complex formation. Figure 3 depicts the corresponding shifts of the protons of **2a** as a function

Scheme 8. Synthesis of the Hamilton-Receptor-Bearing Porphyrin **2b**[a]



[a] Key: (i) EDC, HOBT, DMAP, CH_2Cl_2, 0 °C.

Scheme 9. Syntheses of the Hamilton-Receptor-Bearing Porphyrins **2c**,**d**[a]



[a] Key: (i) $SnCl_2$, acetic acid, reflux; (ii) $ZnOAc_2$, THF, reflux.

of added fullerene derivative **1a**. Additionally, the shifts of the NH^3-protons within the cyanuric acid moiety of **1a** were investigated. In a typical experiment, 0.5 mL of a 1.93 mM solution of porphyrin derivative **2a** was titrated with 100 μL of a 4.3 mM solution of fullerene derivative **1a**. The ^1H NMR spectra were recorded approximately 3 min after mixing the solutions. In each case, the spectrum remained unchanged after 30 min indicating a fast equilibrium formation.

Whereas the NH^1- and NH^2-protons undergo a shift to lower fields, the NH^3-protons of the cyanuric acid moieties at 13 ppm are subject to an opposite effect. The corresponding signals undergo a high-field shift during addition of the fullerene cyanuric acid derivative **1a**. Furthermore, they broaden and, finally, they disappear. The reason for the disappearance in the presence of an excess of **1a** is a fast equilibrium (coalescence

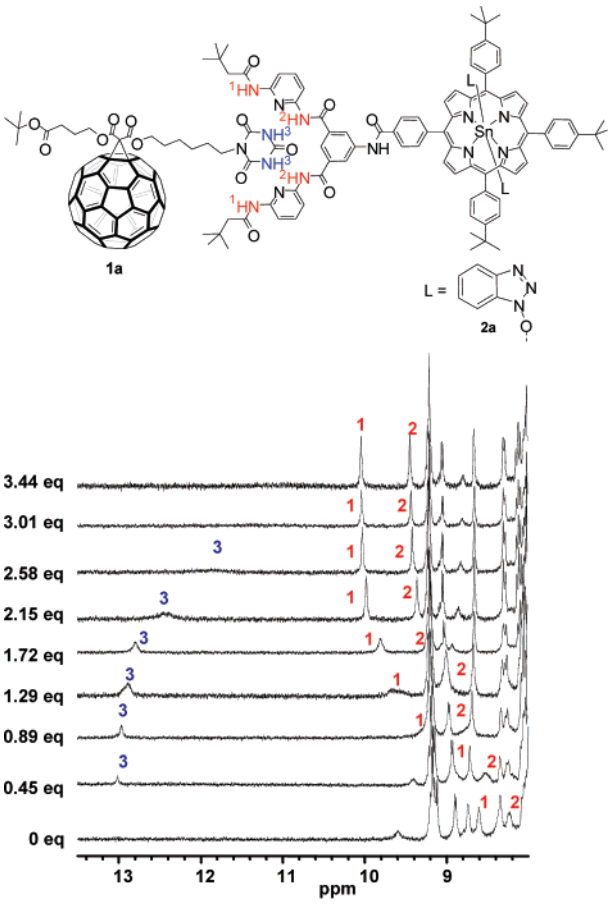


Figure 3. Binding motif between **2a** and **1a** with indication of the NH protons NH^1, NH^2, and NH^3 and ^1H NMR (300 MHz) spectra of **2a** at 1.93 mM in $CDCl_3$ with various equivalents of **1a**.

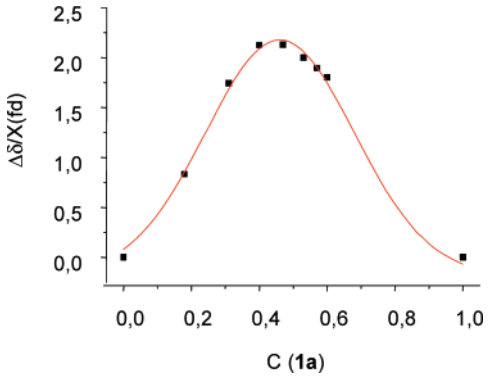


Figure 4. Job's plot analysis of the ^1H NMR (300 MHz) titration of **2a** with **1a** in $CDCl_3$.

regime) between bound and free cyanurate. On the basis of these titration experiments, the association constants K_{ass}. could be determined with the help of the program Chem-Equili.[15] In the case of the complex **1a**·**2a** an association constant K_{ass} of 1.79 $\times$ 10^4 M^{-1} was determined.

In addition, a Job's plot analysis of the titration data was carried out (Figure 4). To this end, the chemical shift variation of NH^1 ($\Delta(\delta)$)was monitored as a function of the molar fraction of the fullerene derivative X(**1a**) and the product of the mole

(15) (a) Solov'ev, V. P.; Vnuk, E. A.; Strakhova, N. N.; Reavsky, O. A. VINITI: Moscow, 1991. (b) Solov'ev, V. P.; Baulin, V. E.; Strahova, N. N.; Kazachenko, V. P.; Belsky, V. K.; Varnek, A. A.; Volkova, T. A.; Wipff, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, *7*, 1489.

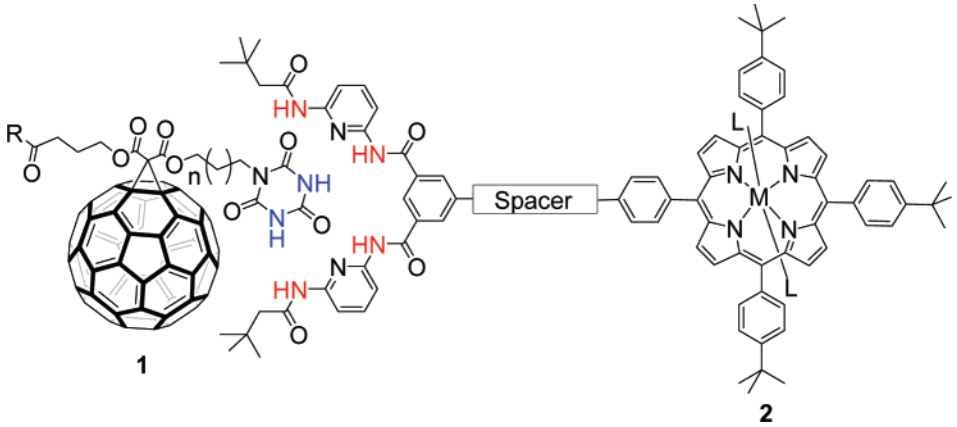


Figure 5. Schematic representation of the titrated compounds.

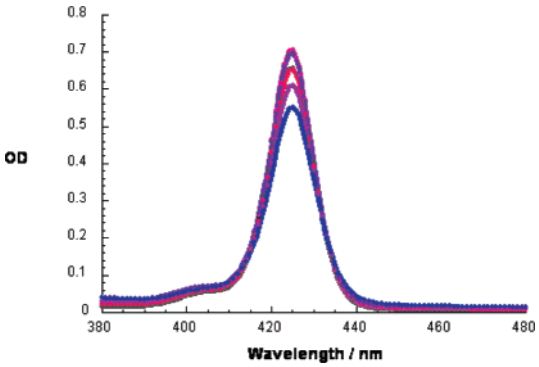


Figure 6. Changes in the Zn porphyrin **2d** (1.9×10^{-6} M) electronic absorption spectrum in toluene upon addition of increasing concentrations of C_{60} derivative **1c** ($(0-2.8) \times 10^{-6}$ M).

fraction X[(fd)$^{-1}$] and $\Delta(\delta)$ was plotted as a function of X. Well in line with the expectation, we found that the fitted curve shows a maximum at 0.5 X(**1a**). Such a finding clearly confirms the existence of a 1:1 stroichiometry.

We found in absorption experiments where Zn porphyrin **2d** and/or Sn porphyrin **2a** solutions (i.e., CH_2Cl_2 or toluene) were titrated (Figure 5) with variable concentrations of C_{60} derivative **1c** (Figure 6), appreciable decreases in the intensity of both Soret- and Q-bands. Moreover, two clear isosbestic points—at 414 and 433 nm—evolve in the titration assays performed with, for example, Zn porphyrin **2d** and C_{60} derivative **1a**, although no overall shift was noted.[16] Such a trend corroborates the NMR experiments, which helped to attest a 1:1 ground state nanohybrid formation between **2a** and/or **2c** and **1a**.

First insights into electron donor−acceptor interactions were derived from complementary fluorescence experiments. The strong fluorescence of Zn porphyrin **2d** ($\Phi_F = 4.0 \times 10^{-2}$) and Sn porphyrin **2a** ($\Phi_F = 3.0 \times 10^{-2}$), which were tested in the absence and presence of variable concentrations of C_{60} derivatives, gives rise to appreciable intrahybrid quenching, when the fullerenes are present.

These dependencies were used to determine the association constants for the formation of the fullerene−porphyrin nanohybrids. In particular, data were taken at the short-wavelength emission maxima of Zn porphyrin **2d** and Sn porphyrin **2a**,

(16) Likewise, a mixture of equimolar quantities of **2a** and /or **2d** and any of the C_{60} derivatives shows an electronic absorption spectrum that differs from the sum spectrum of the parent compounds, thus indicating notable interactions between the donor and the acceptor moieties in the ground state.

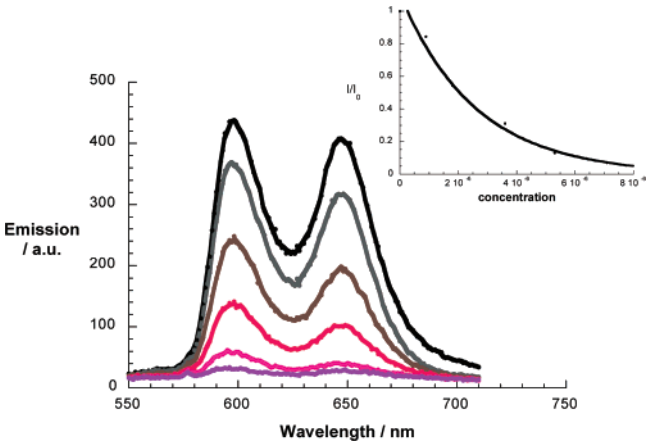


Figure 7. Fluorescence intensity of Zn porphyrin **2d** (1.2×10^{-6} M) in toluene upon addition of increasing amounts of C_{60} compound **1e** ($(0-7.1) \times 10^{-6}$ M).

respectively, and plotted as a function of the fullerene concentration. A nonlinear curve fitting according to eq 1 allowed estimation of the association constants (Figure 7).

$$\frac{I_F}{I_o} = 1 - \frac{1}{2c_D}\left[\frac{1}{K_S} + c_o + c_D - \sqrt{\left(\frac{1}{K_S} + c_o + c_D - 4c_o c_D\right)}\right]$$

In eq 1, I_o refers to the initial fluorescence intensity, c_o is the total porphyrin concentration, c_D is the total concentration of the added fullerene, and K_{ass}. is the association constant. The obtained association constants are summarized in Tables 1 and 2.

All values were estimated on the basis of a 1:1 nanohybrid formation. As was expected, the association constant values increase with decreasing solvent polarity and the substitution of the hexylene alkyl spacer with a propylene spacer in **1e** strengthens the formation of the nanohybrid by a factor of approximately 6.

The fluorescence decays for Zn porphyrin **2d** and Sn porphyrin **2a** were well fitted with monoexponential fitting functions, which gave lifetimes of 1.6 and 0.3 ns in toluene and 1.3 and 0.3 ns in dichloromethane, respectively. However, no fast decaying component, attributed to the complexed Zn porphyrin or Sn porphyrin, was observed after addition of several equivalents of fullerenes. Implicit is that Zn porphyrin **2d** and Sn porphyrin **2a** singlet excited-state deactivation must be faster than the time resolution of our apparatus (i.e., 100 ps).

Table 1. Association Constants (M^{-1}) of the Titrated Assemblies in CH_2Cl_2

porphyrin	fullerene	association constants
2a	**1a**	1.76×10^4
	1b	2.82×10^4
	1c	2.81×10^3
	1d	3.68×10^3
2b	**1a**	2.72×10^4
	1b	7.48×10^4
	1c	7.67×10^4
	1d	5.16×10^4
2c	**1a**	4.42×10^4
	1b	5.34×10^4
	1c	7.21×10^4
	1d	3.63×10^4
2d	**1a**	2.93×10^4
	1b	1.70×10^4
	1c	2.54×10^4
	1d	6.54×10^4

Table 2. Photophysical Parameters Obtained for the Studied Assemblies

		association constants, M^{-1}		quenching efficiency,		
porphyrin	fullerene	toluene	CH_2Cl_2	%	k_q, s^{-1}	τ_s, ns
2c	**1e**	9.2×10^4	2.2×10^4	67	7.80×10^9	0.35(0.08)
	1f	1.9×10^4		27	1.40×10^9	0.31(0.06)
2d	**1c**	1.2×10^5		71	1.55×10^9	
	1e	7.9×10^5	6.2×10^4	87	4.45×10^9	1.7(0.23)
	1f	3.0×10^5	1.2×10^4	75	1.94×10^9	1.3(0.02)

Intrahybrid electron donor−acceptor interactions were confirmed through time-resolved transient absorption measurements, namely, following the photoexcitation of **2d** or **2a** and **2d·1e** or **2a·1e** at 550 and 387 nm respectively in the corresponding references and in the donor−acceptor nanohybrids.[17]

Representative femtosecond time-resolved absorption spectra, taken after a 150 fs laser pulse at 387 or 550 nm in a toluene solution of the **2d** reference, are displayed in Figure 8. The differential spectrum recorded immediately after the laser pulse is characterized by bleaching of the porphyrin Q-band absorptions at 555 and 595 nm as well as broad absorption between 600 and 1100 nm. These spectral attributes are indicative of the ZnP singlet excited state ($E_{Singlet} = 2.00$ eV), which decays slowly (8.3×10^8 s^{-1}) to the energetically lower lying triplet excited state ($E_{Triplet} = 1.53$ eV) via intersystem crossing ($\Phi_{Triplet} = 0.88$). The triplet excited-state features maxima at 475, 580, 625, and 845 nm—with the most important spectral characteristic being the transient peak at 845 nm. Similar, although somewhat faster (3.8×10^9 s^{-1}), is the decay of the SnP singlet excited state ($E_{Singlet} = 1.98$ eV) in **2a** forming the corresponding triplet manifold, for which we noted a characteristic marker at 500 nm; see Figure S1.

Next, the transient absorption changes of **2d·1e** donor−acceptor nanohybrids were recorded in toluene with several time delays after the 550 nm femtosecond laser pulse and compared with what we have noted for the ZnP reference. At early times (i.e., 5−100 ps), these are practically identical with those of the ZnP reference, disclosing strong bleaching at 550 nm. However, at a delay time of 200 ps, a new transition in the visible range around 630 nm grows in (Figure 9) accompanied by another absorption in the near-infrared range—1040 nm. On the basis of a spectral comparison, we ascribe the former to the Zn porphyrin π-radical cation ($ZnP^{\bullet+}$), while the latter band belongs to the fullerene π-radical anion ($C_{60}^{\bullet-}$).

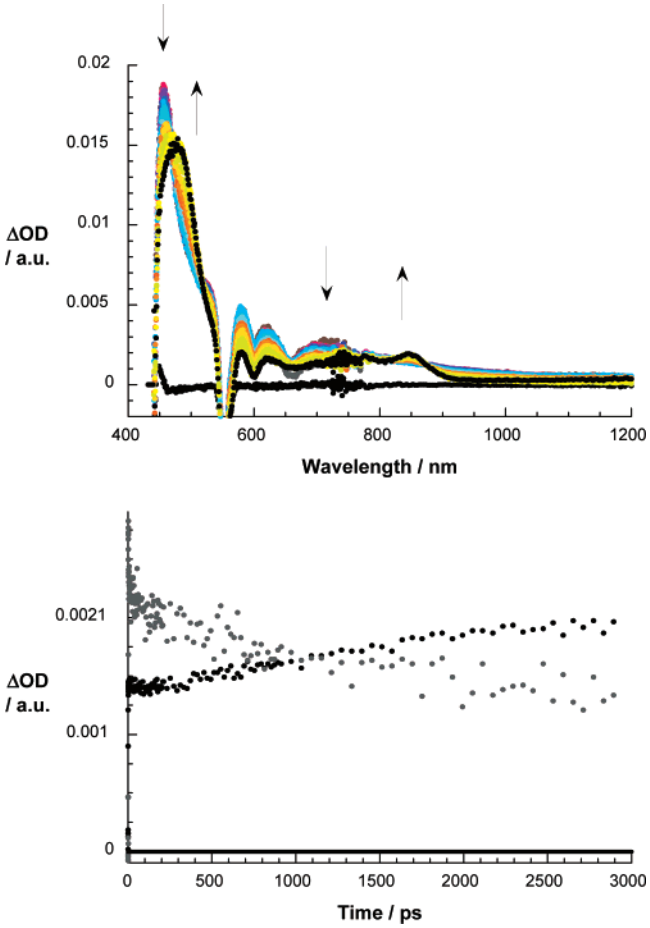


Figure 8. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (550 nm) of Zn porphyrin **2d** in nitrogen-saturated toluene with several time delays. Bottom: Time−absorption profiles of the spectra shown above at 720 (gray spectrum) and 840 (black spetrum) nm, reflecting the formation and decay of the singlet excited state.

In accordance with these results, we propose that charge separation, from the ZnP singlet excited state to the electron-accepting fullerene, creates the $ZnP^{\bullet+}-C_{60}^{\bullet-}$ state, which is responsible for the fast deactivation of the photoexcited chromophore. Analyzing the absorption time profiles, we derive a rate constant of (4.3×10^9 s^{-1}) for the intrahybrid charge separation.

Contrary to the aforementioned ZnP/C_{60} donor−acceptor hybrids, femtosecond photolysis (387 and 550 nm) of the SnP moiety in **2a·1e**, for example, disclosed absorption features that are solely assigned to the C_{60} singlet and triplet excited states with characteristic features at 880 and 740 nm, respectively (Figure 10). In fact, the absence of appreciable radical ion pair absorptions led us to conclude that an unfavorably shifted oxidation potential of about 1 V—when comparing ZnP with SnP (1.44 V in dichloromethane versus SCE)—precludes the anticipated electron transfer.[18] Instead, an exothermic energy transfer process (i.e., 0.22 eV) is the main process of

(17) Although the systems are not fully assembled under the conditions of the experiment, photoexcitation—in particular at 550 nm—allowed us to follow nevertheless the intrahybrid deactivation such as electron and energy transfer.

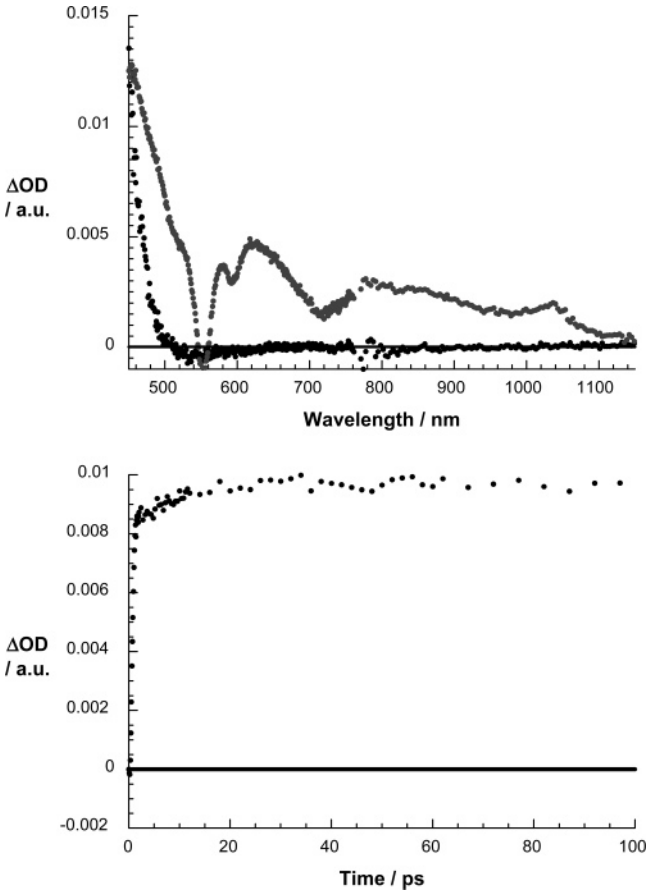


Figure 9. Top: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (550 nm) of Zn porphyrin **2d**/C_{60} compound **1e** in nitrogen-saturated toluene with several time delays (i.e., 0 ps, black spectrum, and 500 ps, brown spectrum). Bottom: Time−absorption profile of the spectra shown above at 620 nm, reflecting the formation of the radical ion pair state.

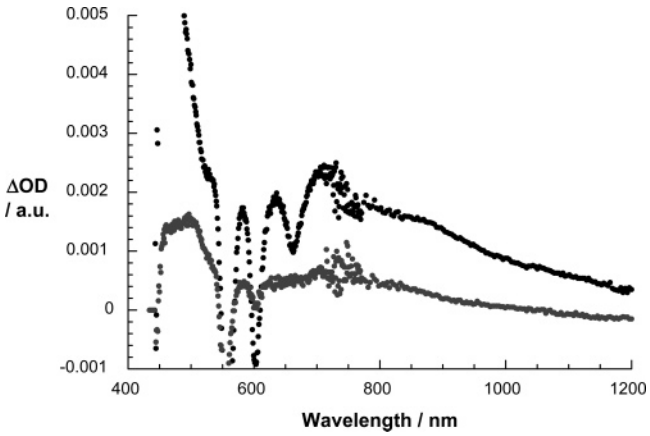


Figure 10. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (550 nm) of Sn porphyrin **2a**/C_{60} compound **1e** in nitrogen-saturated toluene with several time delays (i.e., 50 ps, black spectrum, and 3000 ps, brown spectrum), indicating the formation of fullerene singlet and triplet excited state with transitions at 800 and 740 nm, respectively.

deactivation of the SnP singlet excited state (i.e., to C_{60}) followed by a rapid intersystem crossing to yield the fullerene triplet excited state.

Conclusions

We have investigated for the first time the self-assembly and the photophysical properties of supramolecular fullerene−porphyrin donor−acceptor nanohybrids connected via a Hamilton-receptor based hydrogen bonding motif. In this light, we have synthesized an entire modular set of new C_{60} monoadducts **1** carrying a cyanuric acid terminus within the malonate addend connected via hexylene spacers. These new derivatives complement the structure of previously reported adducts bearing propylene spacers. To overcome the overall poor solubility, especially in solvents where no interference with the hydrogen bonding is expected, we introduced as the second malonate termini a variety of dendritic groups. The Hamilton-receptor counterpart was coupled to a library of porphyrin derivatives involving either tin or zinc as central metals leading to new porphyrin building blocks **2**. The corresponding association constants were determined by NMR and fluorescence tritration experiments. They were found to be in the range between 3.7×10^3 and 7.9×10^5 M^{-1}. Interestingly, the association constants decrease when hexylene instead of propylene spacers are used.

In response to visible light irradiation, the corresponding **2d·1** complexes give rise to a fast charge separation evolving from the photoexcited ZnP chromophores. Time-resolved fluorescence and transient absorption measurements were employed to corroborate this pathway. Most importantly, while the oxidized zinc porphyrin π-radical cation ($ZnP^{\bullet+}$) was identified through its fingerprint absorption in the 550−800 nm range, the signature of the reduced the fullerene π-radical anion ($C_{60}^{\bullet-}$) appeared at 1040 nm. In stark contrast, in the analogous SnP complexes (**2a·1**) energy transfer, instead of electron transfer, occurs from the initially excited SnP excited state to C_{60}. This is due to the shifted oxidation potential when comparing ZnP and SnP.

The most important and unprecedented finding is that electronic communication between the porphyrin donor and fullerene acceptor is even possible through a considerable number of σ and hydrogen bonds. This is expected to open new avenues for the inexpensive and efficient construction of new prototypes of photovoltaic devices.

Experimental Section

General Remarks. Chemicals. C_{60} was obtained from Hoechst AG/Aventis and separated from higher fullerenes by a plug filtration.[19] All chemicals were purchased by chemical suppliers and used without further purification. All analytical reagent-grade solvents were purified by distillation. Dry solvents were prepared using customary literature procedures.[20] Thin layer chromatography (TLC): Riedel-de Haën silica gel F254 and Merck silica gel 60 F254. Detection: UV lamp and iodine chamber. Flash chromatography (FC): Merck silica gel 60 (230−400 mesh, 0.04−0.063 nm). Analytical high-performance liquid chromatography (HPLC): Shimadzu LC-10 liquid chromatograph with Bus modul CBM-10A, auto injector SIL-10A, two pumps LC-10AT, and diode array detector. The HPLC-grade solvents were purchased from

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(19) (a) Reuther, U. Ph.D. Dissertation, University of Erlangen-Nürnberg, Germany, 2002. (b) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231−1250.

(20) Perrin, D. D.; Amarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, U.K., 1988.

SDS or Acros Organics. Analytical column: Nucleosil 5 μm, 200 × 4 mm, Macherey-Nagel, Düren, Germany. Preparative high-performance liquid chromatography (HPLC): Shimadzu Class LC 10 with Bus module CBM-10A, auto injector SIL-10A, two pumps LC-8A, UV detector SPD-10A, and fraction collector FRC-10A. Solvents were purified by distillation prior to use. UV/vis spectroscopy: Shimadzu UV-3102 PC UV/vis/NIR scanning spectrophotometer; absorption maxima λ_{max} given in nm. Mass spectrometry: Micromass Zabspec, FAB (LSIMS) mode, matrix 3-nitrobenzyl alcohol. NMR spectroscopy: JEOL JNM EX 400, JEOL JNM GX 400, and Bruker Avance 300. The chemical shifts are given in ppm relative to TMS. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), and m (multiplet); nonresolved and broad resonances as br. Elemental analysis (C, H, N): succeeded by combustion and gas chromatographical analysis with an EA 1110 CHNS analyzer (CE Instruments). Fluorescence spectroscopy: Flouromax3 Jobin Yvon Horiba, Horiba Jobin Yvon GmbH, München, Germany.

Photophysics. Femtosecond transient absorption studies were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system (Clark-MXR, Inc.). Fluorescence lifetimes were measured with a laser strope fluorescence lifetime spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the laser strobe systems are described on the manufacture's web site. Emission spectra were recorded by using a FluoroMax-3 (Horiba Co.). The experiments were performed at 20 °C.

3-(*tert*-Butoxycarbonyl)propyl 6-Bromohexyl Malonate (4a). A solution of 600 mg (2.45 mmol) of **3**, 299 mg (2.45 mmol) of DMAP, and 364 mg (2.7 mmol) of 1-HOBT in 50 mL of dry CH_2Cl_2 was cooled to 0 °C using an ice bath. Under inert atmosphere, 695 mg (3.37 mmol) of DCC was added and the mixture was stirred at 0 °C for 30 min. Then 551 mg (3.05 mmol) of 6-bromohexane-1-ol was added to the reaction mixture. After another 1 h of stirring at 0 °C, the mixture was allowed to reach room temperature. The reaction progress was controlled using TLC (3:1 hexane/EtOAc). *N*,*N*′-Dicyclohexylurea (DCU) was filtered off after 17 h of stirring, and the solvent was evaporated. The remainder was dissolved in cooled (−16 °C) EtOAc and was then filtered to separate the raw product and DCU. After distillation of the solvent the remainder was purified by flash chromatography (500 mL SiO_2, 3:1 hexane/EtOAc). A 754 mg (1.84 mmol, 75%) amount of a yellow, highly viscous oil was obtained. ^{1}H NMR [$CDCl_3$, 400 MHz, RT (room temperature)] [δ (ppm)]: 1.37 (m, 2H), 1.41 (s, 9H), 1.43 (m, 2H), 1.63 (m, 2H), 1.84 (m, 2H), 1.90 (m, 2H), 2.27 (t, ^3J = 7.10 Hz, 2H), 3.34 (s, 2H), 3.37 (t, ^3J = 7.10 Hz, 2H), 4.11 (t, ^3J = 6.60 Hz, 2H), 4.14 (t, ^3J = 6.60 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.96, 24.95, 27.65, 28.03, 28.23, 31.74, 32.50, 33.60, 41.48, 64.52, 65.34, 80.48, 166.48, 171.93. MS (FAB, NBA): *m*/*z* 408, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 753, 845, 1034, 1096, 1146, 1212, 1254, 1328, 1366, 1393, 1459, 1729, 2864, 2937, 2976. Anal. Calcd for $C_{17}H_{29}O_6Br$ (M_r = 408.11): C, 49.88; H, 7.14. Found: C, 49.62; H, 7.29.

4-(2-((6-Bromohexyloxy)carbonyl)acetoyloxy)butanoic Acid (5). To a solution of 222 mg (0.542 mmol) of **4a** in CH_2Cl_2 was added 4 mL of TFA. This solution was stirred for 2 h. The solvent was distilled, and the remaining yellow oil was dissolved in CH_2Cl_2 again. After removal of the solvent, **5** was obtained as a yellow high viscous oil (190 mg (0.538 mmol, 99%)). ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.35 (m, 2H), 1.44 (m, 2H),1.64 (m, 2H),1.83 (m, 2H), 1.97 (m, 2H), 2.43 (t, ^3J = 7.42 Hz, 2H), 3.35 (s, 2H), 3.36 (t, ^3J = 7.10 Hz, 2H), 4.12 (t, ^3J = 6.55 Hz, 2H), 4.19 (t, ^3J = 6.32 Hz, 2H), 9.65 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.62, 24.96, 27.66, 28.24, 30.25, 32.51, 33.65, 41.47, 64.26, 65.46, 166.48, 166.54, 177.97. MS (FAB, NBA): *m*/*z* 352, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 884, 965,1031, 1096, 1150, 1266, 1332, 1393, 1413, 1729, 1710, 2864, 2941. Anal. Calcd for $C_{13}H_{21}O_6Br$ (M_r = 352.25): C, 44.21; H, 5.99. Found: C, 44.47; H, 6.13.

3-((3,5-Bis(benzyloxy)carbonyl)propyl 6-Bromohexyl Malonate (4b). A 224 mg (0.635 mmol) amount of **5** was added to a solution of 78 mg (0.635 mmol) of DMAP and 94 mg (0.699 mmol) of 1-HOBT in 50 mL of dry CH_2Cl_2. After cooling of the reaction mixture to 0 °C, 180 mg (0.873 mmol) of DCC was added. The reaction mixture was stirred for 30 min until a white precipitate (DCU) attended. To this suspension 254 mg (0.794 mmol) of (3,5-bis(benzyloxy)phenyl)-methanol was added. The suspension was stirred overnight allowing it to reach room temperature. DCU was filtered off, and the solvent was removed under reduced pressure. The remainder was dissolved in cool (−16 °C) EtOAc, and the mixture was then filtered to separate the raw product and DCU. After distillation of the solvent the remainder was purified by flash chromatography (500 mL SiO_2, 3:1 hexane/EtOAc). A 294 mg (0.448 mmol, 71%) amount of a colorless high viscous oil was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.33 (m, 2H), 1.43 (m, 2H), 1.62 (m, 2H), 1.82 (m, 2H), 1.98 (m, 2H), 2.44 (t, ^3J = 7.40 Hz, 2H), 3.34 (s, 2H), 3.37 (t, ^3J = 7.10 Hz, 2H), 4.11 (t, ^3J = 6.87 Hz, 2H), 4.18 (t, ^3J = 6.32 Hz, 2H), 5.01 (s, 2H), 5.03 (s, 4H), 6.56 (s, 2H), 7.39 (m, 10H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.84, 24.98, 27.68, 28.26, 30.57, 32.53, 33.68, 41.48, 64.40, 65.34, 66.22, 70.11, 101.71, 107.08, 128.04, 128.44, 128.61, 136.67, 138.08, 160.09, 166.50, 172.43. MS (FAB, NBA): *m*/*z* 655, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 699, 737, 834, 880, 911, 1027, 1058, 1150, 1216, 1266, 1293, 1324, 1378, 1413, 1451, 1498, 1451, 1498, 1729, 2864, 2937.

Newkome First G-(carbonyl)propyl 6-Bromohexyl Malonate (4c). To a solution of 78 mg (0.637 mmol) of DMAP and 95 mg (0.701 mmol) of 1-HOBT in 50 mL of dry CH_2Cl_2 was added 225 mg (0.637 mmol) of **5**. After the reaction mixture was cooled to 0 °C, 181 mg (0.876 mmol) of DCC was added and the mixture was stirred for 30 min until a white precipitate (DCU) attended. To this suspension was added 334 mg (0.796 mmol) of di-*tert*-butyl 4-(2-*tert*-butoxycarbonyl)-ethyl)-4-aminoheptanedioate, and the mixture was stirred overnight allowing it to reach room temperature. DCU was filtered off, and the solvent was distilled. After the yellowish remainder was dissolved in cool (−16 °C) EtOAc and the remaining DCU was separated from the solution, the solvent was removed in vacuum. The remaining yellow oil was purified using flash chromatography (400 mL of SiO_2, 2:1 hexane/EtOAc). A 268 mg (0.355 mmol, 56%) amount of a colorless high viscous oil was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.33 (m, 2H), 1.41 (s, 27H), 1.44 (m, 2H), 1.61 (m, 2H), 1.85 (m, 2H), 1.94 (m, 8H), 2.17 (t, ^3J = 7.81 Hz, 2H), 2.19 (t, ^3J = 7.32 Hz, 6H), 3.37 (s, 2H), 4.13 (t, ^3J = 6.59 Hz, 2H), 4.16 (t, ^3J = 6.23 Hz, 2H), 6.56 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.66, 24.99, 27.71, 28.05, 28.27, 29.79, 32.29, 32.54, 33.65, 41.47, 57.45, 64.50, 65.54, 80.63, 166.47, 166.91, 171.21, 172.85. MS (FAB, NBA): *m*/*z* 752, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 757, 849, 953, 1031, 1104, 1146, 1216, 1254, 1316, 1366, 1393, 1420, 1459, 1536, 1660, 1679, 1725, 2937, 2980.

(*R*,*R*)-1,2-Bis((benzyloxy)carbonyl)-2-oxyethylbenzoate 6-Bromohexyl Malonate (4d). After preparation of a solution of 104 mg (0.85 mmol) of DMAP and 126 mg (0.94 mmol) of 1-HOBT in 50 mL of dry CH_2Cl_2, 300 mg (0.85 mmol) of **5** was added. After cooling of the reaction mixture to 0 °C, DCC (241 mg (1.17 mmol)) was added. The mixture was stirred for 30 min before 462 mg (1.06 mg) of (*R*,*R*)-1,2-bis(benzyloxy)carbonyl)-2-hydroxethyl benzoate was added. The suspension was stirred overnight reaching room temperature. After filtration the remaining solution was concentrate in vacuum. After the appearance of DCU, cool (−16 °C) ethyl acetate was given to the suspension to separate DCU from the main product. Ethyl acetate was removed in vacuum, and the remainder must be purified by flash chromatography (400 mL SiO_2, 95:5 CH_2Cl_2/EtOAc). A 580 mg (0.75 mmol, 89%) amount of white crystals was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz,

RT) [δ (ppm)]: 1.36 (m, 2H), 1.43 (m, 2H), 1.64 (m, 2H), 7.93 (m, 2H), 1.87 (m, 2H), 7.38 (m, 2H), 2.36 (m, 2H), 2.41 (m, 2H), 3.36 (s, 2H), 3.37 (t, ^3J = 6.00 Hz, 2H), 4.12 (t, ^3J = 6.60 Hz, 4H), 5.13 (d, ^2J = 11.55 Hz, 4H), 5.82 (d, ^2J = 2.20 Hz, 1H), 5.91 (d, ^2J = 2.10 Hz, 1H), 7.30 (m, 4H), 7.40 (m, 4H), 7.42 (m, 2H), 7.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.60, 24.97, 27.68, 28.26, 29.87, 32.53, 33.66, 41.45, 64.11, 65.43, 67.62, 70.96, 71.14, 128.39, 128.44, 128.48, 128.62, 130.07, 133.65, 134.46, 134.84, 164.99, 165.49, 166.45, 166.50, 171.32. MS (FAB, NBA): *m*/*z* 771, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 714, 803, 826, 849, 907, 949, 1027, 1069, 1096, 1131, 1193, 1258, 1332, 1382, 1455, 1602, 1729, 2957.

6-Bromohexyl Methyl Malonate (4e). A solution of 300 mg (1.66 mmol) of 6-bromohexane-1-ol in 35 mL of dry CH_2Cl_2 was prepared, and 134 μL (1.66 mmol) of pyridine was added before the reaction mixture was cooled to 0 °C. During 1.5 h, a solution of 178 μL (1.66 mmol) of methyl malonyl chloride in 20 mL of dry CH_2Cl_2 was added dropwise. After stirring of the solution overnight (0 °C → RT), the organic layer was washed three times with 80 mL of water and dried over $MgSO_4$. The solvent was distilled in vacuum, and the yellow remainder was purified using flash chromatography (350 mL of SiO_2, 3:1 hexane/EtOAc). A 400 mg (1.42 mmol, 86%) amount of a viscous oil was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.36 (m, 2H), 1.45 (m, 2H), 1.65 (m, 2H), 1.84 (m, 2H), 3.36 (s, 2H), 3.39 (t, ^3J = 6.71 Hz, 2H), 3.73 (s, 3H), 4.13 (t, ^3J = 6.59 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.97, 27.68, 28.25, 32.54, 33.63, 41.35, 52.49, 65.40, 166.53, 167.00. MS (FAB, NBA): *m*/*z* 281, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 687, 730, 849, 1023, 1146, 1200, 1270, 1336, 1390, 1413, 1436, 1733, 2864, 2941.

6-Bromohexyl Ethyl Malonate (4f). To a solution of 300 mg (1.66 mmol) of 6-bromohexane-1-ol in 35 mL of dry CH_2Cl_2 was added 134 μL (1.66 mmol) of pyridine before the reaction mixture was cooled to 0 °C. Then a solution of 235 μL (1.82 mmol) of ethyl malonyl chloride in 20 mL of dry CH_2Cl_2 was dropped into the reaction mixture during 1.5 h. The solution was stirred overnight (0 °C → RT), and the organic layer was washed three times with 100 mL water and dried over $MgSO_4$. After distillation of the solvent in vacuum, the yellow residue was purified using flash chromatography (350 mL of SiO_2, 3:1 hexane/EtOAc). A 440 mg (1.49 mmol, 90%) amount of of a viscous oil was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.26 (t, ^3J = 7.15 Hz, 3H), 1.37 (m, 2H), 1.45 (m, 2H), 1.65 (m, 2H), 1.84 (m, 2H), 3.35 (s, 2H), 3.39 (t, ^3J = 6.87 Hz, 2H), 4.13 (t, ^3J = 6.60 Hz, 2H), 4.18 (q, ^3J = 7.15 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 14.07, 24.99, 27.70, 28.28, 32.56, 33.62, 41.65, 61.50, 65.33, 166.57, 166.65. MS (FAB, NBA): *m*/*z* 295, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 683, 730, 849, 992, 1031, 1146, 1185, 1224, 1266, 1332, 1370, 1390, 1413, 1463, 1729, 2864, 2941.

Monoadduct 6a. Under inert conditions 474 mg (0.659 mmol) of C_{60} was dissolved in 200 mL of toluene and the solution was stirred for 45 min at room temperature and exclusion of light. After C_{60} had dissolved, 127 mg (0.384 mmol) of CBr_4 and 150 mg (0.366 mmol) of **4a** were added. A solution of 113 μL (0.732 mmol) of DBU in toluene was added dropwise during a period of 1 h. After stirring of the solution for another 1 h at room temperature and exclusion of light, the reaction mixture was concentrated and surplus C_{60} was removed using flash chromatography (500 mL of SiO_2, 100% toluene). **8** was achieved by flash chromatography (500 mL SiO_2, 100% toluene) as bordeaux oil. The oil was dissolved in a small amount of CH_2Cl_2 and precipitated using fresh distilled *n*-pentane. The brownish crystals (194 mg, 0.172 mmol, 47%) were removed using a centrifuge. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 0.86 (m, 2H), 1.43 (m, 2H), 1.45 (s, 9H), 1.46 (m, 2H), 1.84 (m, 2H), 2.11 (m, 2H), 2.41 (t, ^3J = 7.10 Hz, 2H), 3.40 (t, ^3J = 7.10 Hz, 2H), 4.49 (t, ^3J = 6.60 Hz, 2H), 4.51 (t, ^3J = 6.60 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.10, 25.19, 27.69, 28.14, 28.40, 31.68, 33.65, 52.14, 64.52, 66.34, 67.20, 71.50, 80.75, 138.97, 140.96, 141.85, 141.88, 142.18, 142.98, 143.00, 143.06, 143.86, 144.61, 144.67, 144.88, 145.10, 145.17, 145.20, 145.26, 163.58, 171.14. MS (FAB, NBA): *m*/*z* 1128, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 760, 799, 956, 1056, 1205, 1231, 1395, 1725, 2850, 2935. UV/vis (CH_2Cl_2) [λ (nm)]: 254, 325, 425.5.

Monoadduct 6b. C_{60} (474 mg (0.659 mmol)) was dissolved in 150 mL of toluene under exclusion of light and air during 45 min. Then 137 mg (0.384 mmol) of CBr_4 and 240 mg (0.366 mmol) of **4b** were added before 111 mg (109 μL (0.732 mmol)) of DBU, dissolved in toluene, was added dropwise during 1 h. After 2 h of stirring at room temperature and under exclusion of air and light, the reaction mixture was concentrated and then purified by flash chromatography (350 mL of SiO_2, toluene → 9:1 toluene/EtOAc). The obtained red solid was dissolved in a small amount of CH_2Cl_2 and then precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 250 mg (0.182 mmol, 48%) of brown solid was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.46 (m, 2H), 1.47 (m, 2H), 1.53 (m, 2H), 1.81 (m, 2H), 2.17 (m, 2H), 2.58 (t, ^3J = 7.42 Hz, 2H), 3.37 (t, ^3J = 6.87 Hz, 2H), 4.47 (t, ^3J = 6.60 Hz, 2H), 4.54 (t, ^3J = 6.32 Hz, 2H), 5.04 (s, 2H), 5.06 (s, 2H), 6.57 (s, 3H), 7.38 (m, 10H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.98, 24.98, 25.16, 28.40, 30.55, 32.57, 33.65, 52.17, 66.15, 66.39, 67.24, 70.12, 71.49, 101.74, 107.16, 127.54, 128.06, 128.61, 136.64, 137.97, 138.82, 139.05, 140.93, 140.96, 141.81, 142.16, 142.95, 143.07, 143.83, 143.86, 144.59, 144.67, 144.87, 145.03, 145.08, 145.12, 145.17, 145.21, 145.24, 160.10, 163.52, 172.23. MS (FAB, NBA): *m*/*z* = 1374 $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 676, 710, 760, 780, 830, 926, 1150, 1204, 1231, 1737. UV/vis (CH_2Cl_2) [λ (nm)]: 223, 230.5, 258, 326, 426.5.

Monoadduct 6c. During 45 min, 426 mg (0.591 mmol) of C_{60} was dissolved in 250 mL of toluene under exclusion of light and air. Then 115 mg (0.245 mmol) of CBr_4 and 248 mg (0.329 mmol) of **4c** were added before 100 mg (98 μL (0.658 mmol)) of DBU, dissolved in toluene, was added dropwise during 2.5 h. After 1.5 h of stirring at room temperature and under exclusion of light and air, the reaction mixture was concentrated and purified by flash chromatography (350 mL of SiO_2, toluene → 9:1 toluene/EtOAc). The obtained red brown solid was dissolved in a small amount of CH_2Cl_2 and then precipitated using *n*-pentane. After centrifugation, decantation, and drying, 203 mg (0.138 mmol, 42%) of a brown powder appeared. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.38 (m, 2H), 1.42 (s, 27H), 1.50 (m, 2H), 1.57 (m, 2H), 1.86 (m, 2H), 1.95 (m, 2H), 1.97 (m, 6H), 2.21 (t, ^3J = 7.82 Hz, 2H), 2.29 (t, ^3J = 7.69 Hz, 6H), 3.40 (t, ^3J = 6.71 Hz, 2H), 4.49 (t, ^3J = 6.47 Hz, 2H), 4.52 (t, ^3J = 6.34 Hz, 2H), 6.02 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.62, 25.21, 27.70, 28.08, 28.42, 29.84, 30.02, 32.58, 33.70, 52.24, 57.55, 66.57, 67.30, 71.53, 80.73, 138.95, 138.98, 140.96, 140.99, 141.85, 141.87, 142.16, 143.00, 143.02, 143.11, 143.89, 144.65, 144.69, 144.90, 145.12, 145.19, 145.26, 145.28, 163.54, 163.77, 172.84, 170.78. MS (FAB, NBA): *m*/*z* 1465, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 706, 726, 787, 849, 876, 931, 950, 992, 1011, 1054, 1100, 1150, 1231, 1293, 1366, 1390, 1428, 1455, 1529, 1679, 1702, 1725. UV/vis (CH_2Cl_2) [λ (nm)]: 258, 325.5, 425.5.

Monoadduct 6d. C_{60} (542 mg (0.752 mmol)) was dissolved in 300 mL of toluene during 45 min before 105 mg (0.414 mmol) of I_2 and 290 mg (0.376 mmol) of **4d** were added under inert atmosphere and exclusion of light. A solution of DBU [62 μL (0.414 mmol)] in toluene was added dropwise over a period of 0.5 h. Afterward the reaction mixture was stirred for 2.5 h. The product was extracted by flash chromatography (300 mL SiO_2, toluene → 95:5 toluene/EtOAc). The appearing dark red solid was dissolved in a small amount of CH_2Cl_2 and precipitated with *n*-pentane. After centrifugation, decantation, and drying, 270 mg (0.184 mmol, 48%) of black powder appeared. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.27 (m, 2H), 1.54 (m, 2H), 1.81 (m, 2H), 2.07 (m, 2H), 2.37 (m, 2H), 2.49 (t, ^3J = 7.14 Hz, 2H), 3.35 (t, ^3J = 6.60 Hz, 2H), 4.12 (t, ^3J = 6.32 Hz, 4H), 5.14 (d, ^2J = 3.42 Hz, 2H), 5.27 (d, ^2J = 3.54 Hz, 2H), 5.86 (d, ^2J = 2.20 Hz, 1H), 5.92

(d, ^2J = 2.10 Hz, 1H), 7.10 (m, 4H), 7.33 (m, 4H), 7.18 (m, 2H), 7.41 (m, 2H), 7.56 (m,1H), 7.92 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.78, 25.15, 27.66, 28.41, 29.88, 32.57, 33.68, 52.14, 65.92, 67.29, 67.80, 67.97, 71.04, 71.14, 71.50, 128.33, 128.38, 128.51, 128.67, 130.05, 133.69, 134.86, 134.84, 138.98, 140.96, 140.99, 141.84, 141.89, 142.19, 143.00, 143.07, 143.27, 143.41, 142.88, 144.06, 144.63, 144.68, 144.90, 145.09, 145.14, 145.20, 145.26, 145.49, 145.85, 146.57, 146.70, 146.98, 163.49, 164.98, 165.11, 165.48, 171.11. MS (FAB, NBA): *m*/*z* 1488, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 732, 799, 899, 926, 972, 1015, 1054, 1092, 1131, 1204, 1231, 1702, 1733. UV/vis (CH_2Cl_2) [λ (nm)]: 217, 228.5, 258.5, 327, 425.5.

Monoadduct 6e. A solution of 1.024 g (1.423 mmol) of C_{60} in 350 mL of toluene was prepared under inert atmosphere and exclusion of light. I_2 (199 mg (0.782 mmol)) and **4e** (200 mg (0.711 mmol)) were added to the solution before 138 μL (0.924 mmol) of DBU in toluene was carefully dropped into the solution during 2.5 h. After stirring of the solution for 2 h, the product was isolated using flash chromatography (350 mL of SiO_2, 2:1 toluene/hexane). The appeared dark brown solid was dissolved in a minimal amount of CH_2Cl_2 and precipitated with *n*-pentane. After centrifugation, decantation, and drying, 413 mg (0.413 mmol, 58%) of a brown powder was isolated. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.50 (m, 2H), 1.51 (m, 2H), 1.53 (m, 2H), 1.85 (m, 2H), 3.40 (t, ^3J = 6.71 Hz, 2H), 4.08 (s, 3H), 4.49 (t, ^3J = 6.47 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 25.18, 27.69, 28.39, 32.59, 33.65, 52.08, 54.02, 67.19, 71.48, 138.86, 139.12, 140.96, 141.87, 141.92, 142.19, 142.97, 143.01, 143.09, 143.88, 144.63, 144.69, 144.89, 145.08, 145.11, 145.14, 145.19, 145.27, 163.59, 164.11. MS (FAB, NBA): *m*/*z* 998, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 703, 726, 795, 876, 930, 1000, 1038, 1058, 1112, 1185, 1208, 1231, 1428, 1640, 1671, 1698, 1741. UV/vis (CH_2Cl_2) [λ (nm)]: 255, 326.5, 425.5.

Monoadduct 6f. After preparation of a solution of 1.073 g (1.49 mmol) of C_{60} in 300 mL of toluene, 208 mg (0.82 mmol) of I_2 and 220 mg (0.745 mmol) of **4f** were added under inert atmosphere and exclusion of light. DBU (144 μL (0.97 mmol) in toluene was carefully dropped to the solution during 2 h. After stirring of the solution for another 2 h, the product was extracted using flash chromatography (350 mL of SiO_2, 2:1 toluene/hexane). The occurring brown solid was dissolved in a tiny amount of CH_2Cl_2 and precipitated with *n*-pentane. After centrifugation, decantation, and drying, 290 mg (0.286 mmol, 38%) of a brown powder could be isolated. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.47 (t, ^3J = 6.97 Hz, 3H), 1.49 (m, 2H), 1.50 (m, 2H), 1.53 (m, 2H), 1.85 (m, 2H), 3.40 (t, ^3J = 6.60 Hz, 2H), 4.54 (t, ^3J = 7.15 Hz, 2H), 4.56 (q, ^3J = 7.15 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 14.30, 25.21, 27.73, 28.43, 32.60, 33.63, 52.26, 63.45, 67.15, 71.60, 138.90, 139.10, 140.96, 141.91, 142.21, 143.01, 143.09, 143.88, 144.62, 144.68, 144.88, 145.14, 145.18, 145.26, 143.35, 163.57, 163.67. MS (FAB, NBA): *m*/*z* 1014, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 695, 791, 938, 1004, 1058, 1112, 1177, 1231, 1266, 1428, 1737. UV/vis (CH_2Cl_2) [λ (nm)]: 256, 327, 426.

Monoadduct 1a. Cyanuric acid (183 mg (1.42 mmol)) was dissolved in 25 mL of dry DMF before 11 μL (0.071 mmol) of DBU was added and the reaction mixture was heated to 40 °C. Under inert atmosphere and exclusion of light, 80 mg (0.071 mmol) of **6a** was added. The solution was stirred for 6 h under these conditions before 100 mL of H_2O was added and the organic compounds were extracted with CH_2Cl_2. After washing of the organic layer three times with 100 mL of H_2O and drying over $MgSO_4$, the product could be isolated by flash chromatography (250 mL of SiO_2, 1:1 CH_2Cl_2/EtOAc). The appearing dark solid was dissolved in a minimum amount of CH_2Cl_2 and precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 15 mg (0.013 mmol, 18%) of a brown powder appeared. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.42 (m, 2H), 1.43 (m, 2H), 1.45 (s, 9H), 1.63 (m, 2H), 1.84 (m, 2H), 2.11 (m, 2H), 2.41 (t, ^3J = 7.42 Hz, 2H), 3.83 (t, ^3J = 7.42 Hz, 2H), 4.49 (t, ^3J = 6.60 Hz, 2H), 4.51 (t, ^3J = 6.60 Hz, 2H), 8.79 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.13, 25.45, 26.03, 27.61, 28.15, 28.34, 31.78, 41.74, 52.21, 66.41, 67.24, 71.55, 80.96, 138.98 140.95, 141.86, 141.98, 142.19, 142.98, 143.01, 143.07, 143.86, 144.60, 144.67, 144.88, 145.14, 145.18, 145.26, 147.34, 148.81, 163.57, 172.11. MS (FAB, NBA): *m*/*z* 1175, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 760, 799, 856, 923, 982, 1009, 1143, 1231, 1352, 1388, 1420, 1553, 1688, 1725. UV/vis (CH_2Cl_2) [λ (nm)]: 257, 326.5, 425.

Monoadduct 1b. Cyanuric acid (147 mg (1.136 mmol)) was dissolved in 40 mL of dry DMF under inert atmosphere before 9 μL (0.057 mmol) of DBU was added. After heating of the solution to 40 °C, 78 mg (0.057 mmol) of **6b** was added to the mixture. After being stirred for 5 h under inert atmosphere and exclusion of light, the mixture was quenched by adding 100 mL of H_2O and the product was extracted with 100 mL of CH_2Cl_2. The organic layer was washed three times with 100 mL of H_2O, dried over $MgSO_4$, and purified by flash chromatography (250 mL of SiO_2, 1:1 CH_2Cl_2/EtOAc). The obtained red brown solid was dissolved in a small amount of CH_2Cl_2 and precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 15 mg (0.011 mmol, 19%) of a brown powder could be isolated. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.39 (m, 2H), 1.48 (m, 2H), 1.55 (m, 2H), 1.81 (m, 2H), 2.17 (m, 2H), 2.56 (t, ^3J = 7.15 Hz, 2H), 3.80 (t, ^3J = 7.42 Hz, 2H), 4.46 (t, ^3J = 6.60 Hz, 2H), 4.54 (t, ^3J = 6.32 Hz, 2H), 5.00 (s, 2H), 5.06 (s, 4H), 6.57 (s, 1H), 6.58 (s, 2H), 7.38 ((m(, 10H), 8.16 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.96, 25.43, 26.01, 28.32, 30.61, 34.85, 41.74, 52.16, 66.21, 66.44, 67.24, 70.25, 71.50, 101.74, 107.19, 127.56, 128.06, 128.61, 136.64, 137.99, 136.64, 137.99, 138.79, 139.10, 140.93, 141.83, 142.16, 142.96, 143.85, 144.61, 144.88, 145.04, 145.12, 145.17, 145.23, 146.67, 148.49, 160.07, 163.57, 165.58, 172.52. MS (FAB, NBA): *m*/*z* 1422, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 672, 688, 733, 795, 834, 880, 907, 942, 961, 1004, 1054, 1089, 1146, 1173, 1208, 1227, 1320, 1347, 1386, 1428, 1455, 1540, 1559, 1602, 1702, 1725, 1961, 1980, 2007, 2034, 2081, 2131, 2169, 2189, 2243, 2277, 2853, 2922, 2941. UV/vis (CH_2Cl_2) [λ (nm)]: 220.5, 232, 255, 328.5, 425.

Monoadduct 1c. Cyanuric acid (145 mg (1.12 mmol)) was dissolved in 35 mL of dry DMF before 8.5 μL (0.056 mmol) of DBU was added under inertatmosphere. After heating of the solution to 40 °C, 83 mg (0.056 mmol) of **6c** was added. The reaction mixture was stirred for 6 h under inert atmosphere and exclusion of light. The reaction temperature was 40 °C. When no change in progress was noticed, the reaction mixture was quenched by 100 mL of H_2O and the organic compounds were extracted with 100 mL of CH_2Cl_2. After washing of the organic layer three times with 100 mL of H_2O, it was dried over $MgSO_4$. The product could by isolated by flash chromatography (120 mL of SiO_2, 2:1 CH_2Cl_2/EtOAc). The occurring dark red solid was dissolved in a minimum amount of CH_2Cl_2 and precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 12 mg (0.008 mmol, 14%) of a brown powder appeared. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.38 (m, 2H), 1.41 (s, 27H), 1.50 (m, 2H), 1.54 (m, 2H), 1.65 (m, 2H), 1. 99 (m, 2H), 2.19 (m, 6H), 2.21 (t, ^3J = 7.32 Hz, 2H), 2.33 (t, ^3J = 7.08 Hz, 6H), 3.85 (t, ^3J = 7.32 Hz, 2H), 4.49 (t, ^3J = 6.00 Hz, 2H), 4.50 (t, ^3J = 6.47 Hz, 2H), 6.18 (broad s, 1H), 9.16 (broad s, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 24.73, 25.98, 27.58, 28.08, 28.32, 29.90, 30.08, 33.27, 41.57, 52.12, 57.60, 66.71, 67.13, 71.54, 80.98, 138.78, 139.29, 140.93, 140.96, 141.86, 141.92, 142.19, 143.01, 143.07, 143.88, 144.62, 144.67, 144.88, 145.07, 145.11, 145.17, 145.26, 147.37, 149.13, 163.58, 163.66, 171.34, 173.19. MS (FAB, NBA): *m*/*z* 1518, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 705, 751, 746, 845, 961, 1031, 1069, 1116, 1154, 1189, 1258, 1285, 1305, 1390, 1463, 1536, 1613, 1687, 1729, 1768. UV/vis (CH_2Cl_2) [λ (nm)]: 254.5, 326.5, 426.

Monoadduct 1d. Cyanuric acid (121 mg (0.94 mmol)) was dissolved in 40 mL of dry DMF before 7.2 mg (0.047 mmol) of DBU was added, and the reaction mixture was heated to 40 °C. Under inert atmosphere and exclusion of light, 70 mg (0.046 mmol) of **6d** was added. The

solution was stirred for 4.5 h under the same conditions and was quenched by adding 100 mL of H_2O afterward. To extract the organic compounds, 100 mL of CH_2Cl_2 was added. The organic layer was washed three times with 100 mL of H_2O and dried over $MgSO_4$. The product could be isolated by flash chromatography (150 mL SiO_2, 3:1 CH_2Cl_2/EtoAC). The occurring dark red solid was dissolved in a small amount of CH_2Cl_2 and precipitated with *n*-pentane. After centrifugation, decantation, and drying, 10 mg (0.007 mmol, 14%) of a dark brown powder appeared. ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.23 (m, 2H), 1.58 (m, 2H), 1.82 (m, 2H), 2.19 (m, 2H), 2.35 (m, 2H), 2.48 (t, ^3J = 6.84 Hz, 2H), 3.80 (t, ^3J = 7.69 Hz, 2H), 4.47 (t, ^3J = 6.23 Hz, 2H), 4.48 (t, ^3J = 6.47 Hz, 2H), 5.16 (d, ^2J = 8.18 Hz, 4H), 5.87 (d, ^2J = 2.90 Hz, 1H), 5.93 (d, ^2J = 2.80 Hz, 1H), 7.08 (m, 4H), 7.17 (m, 2H), 7.34 (m, 4H), 7.40 (m, 2H), 7.56 (m, 1H), 7.91 (m, 2H), 8.35 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 23.65, 24.16, 26.03, 27.59, 29.88, 33.68, 41.72, 52.14, 66.95, 67.88, 67.98, 68.07, 71.15, 71.52, 71.60, 128.33, 128.37, 128.49, 128.67, 130.07, 133.71, 134.41, 134.82, 138.90, 138.99, 139.10, 140.95, 141.89, 142.19, 142.54, 142.98, 143.01, 143.88, 144.62, 144.68, 144.90, 145.09, 145.18, 145.26, 146.40, 146.79, 148.55, 150.06, 164.99, 164.63, 165.11, 165.66, 171.27. MS (FAB, NBA): *m*/*z* 1536, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 710, 741, 869, 907, 965, 1004, 1027, 1069, 1116, 1189, 1270, 1332, 1382, 1436, 1498, 1602, 1691, 1745. UV/vis (CH_2Cl_2) [λ (nm)]: 256.5, 324, 426.5.

Monoadduct 1e. Cyanuric acid (336 mg (2.6 mmol)) was dissolved in 40 mL of dry DMF before 20 mg (0.13 mmol) of DBU was added, and the solution was heated to 40 °C. Under inert atmosphere and exclusion of light, 130 mg (0.13 mmol) of **6e** was added. To increase the solubility, 5 mL of dry CH_2Cl_2 was added. The reaction mixture was stirred for 5 h under these conditions. Then 100 mL of H_2O was added and the organic compounds were extracted with 100 mL of CH_2Cl_2. The organic layer was washed three times with 100 mL of H_2O and dried over $MgSO_4$. The product could be isolated by flash chromatography (100 mL of SiO_2, CH_2Cl_2). The appearing black solid was dissolved in a small amount of CH_2Cl_2/THF and precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 14 mg (0.013 mmol, 10%) of a brown powder attended. ^{1}H NMR ($CDCl_3$/THF-d_8, 400 MHz, RT) [δ (ppm)]: 1.37 (m, 2H), 1.47 (m, 2H), 1.62 (m, 2H), 1.82 (m, 2H), 3.79 (t, ^3J = 7.42 Hz, 2H), 4.04 (s, 3H), 4.45 (t, ^3J = 6.32 Hz, 2H), 9.95 (s, 2H). ^{13}C NMR ($CDCl_3$/THF_{d8}, 400 MHz, RT) [δ (ppm)]: 26.18, 27.71, 28.34, 30.73, 41.36, 52.06, 53.93, 67.27, 71.46, 138.82, 139.04, 140.89, 141.80, 141.84, 142.12, 142.92, 142.98, 143.80, 144.53, 144.61, 144.80, 145.03, 145.11, 145.18, 145.24, 147.89, 149.39, 163.47, 164.01. MS (FAB, NBA): *m*/*z* 1048, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 710, 737, 764, 795, 857, 938, 907, 999, 1061, 1116, 1185, 1235, 1266, 1397, 1428, 1463, 1559, 1594, 1687, 1741. UV/vis (CH_2Cl_2/THF) [λ (nm)]: 251.5, 325.5, 426.

Monoadduct 1f. To a solution of 271 mg (2.1 mmol) of cyanuric acid in 40 mL of dry DMF was added 16 mg (0.105 mmol) of DBU. After heating the solution to 40 °C, 106 mg (0.105 mmol) of **6f** was added under inert atmosphere and exclusion of light. To increase the solubility, 5 mL of dry CH_2Cl_2 was added. After the solution was stirred for 6 h under these conditions, 100 mL of H_2O was added and the organic compounds were extracted with 100 mL of CH_2Cl_2. The organic layer was washed three times with 100 mL of H_2O and dried over $MgSO_4$. The product could be isolated by flash chromatography (100 mL of SiO_2, CH_2Cl_2). The occurring dark brown solid was dissolved in a small amount of CH_2Cl_2/THF and precipitated by adding *n*-pentane. After centrifugation, decantation, and drying, 11 mg (0.01 mmol, 10%) of a brown powder appeared. ^{1}H NMR ($CDCl_3$/THF-d_8, 400 MHz, RT) [δ (ppm)]: 1.24 (m, 2H), 1.37 (m, 2H), 1.43 (t, ^3J = 7.08 Hz, 3H), 1.61 (m, 2H), 2.04 (m, 2H), 3.76 (t, ^3J = 7.57 Hz, 2H), 4.43 (t, ^3J = 7.20 Hz, 2H), 4.51 (t, ^3J = 7.00 Hz, 2H), 10.02 (s,2H). ^{13}C NMR ($CDCl_3$/THF-d_8, 100.5 MHz, RT) [δ (ppm)]: 14.17, 25.51, 26.21, 27.70, 28.37, 41.33, 52.21, 63.35, 67.62, 71.55, 140.84, 141.81, 142.12, 142.91, 142.98, 143.78, 144.03, 144.51, 144.59, 144.78, 145.08, 145.12, 145.15, 145.21, 145.31, 147.84, 149.42, 163.46, 163.55. MS (FAB, NBA): *m*/*z* 1062, $[M]^+$. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 772, 791, 861, 926, 969, 1011, 1061, 1116, 1189, 1235, 1270, 1289, 1386, 1432, 1467, 1741. UV/vis (CH_2Cl_2/THF) [λ (nm)]: 254, 327, 426.

5-(*p*-Carboxymethyphenyl)-10,15,20-(*p*-*tert*-butyltriphenyl)porphyrin (8). A solution of 6.8 mL of pyrrole (0.10 mol), 12.6 mL of 4-*tert*-butylbenzaldehyde (0.075 mol), 4.10 g of methyl 4-formylbenzoate (0.025 mol), 20 mL of ethanol, and 100 mg of tetraphenylphosphonium chloride in 2.5 L of dichloromethane was stirred for 30 min. Then 6.3 mL of boron trifluoride etherate (0.049 mol) was added changing the color of the solution to purple red. The mixture was stirred for at least 35 min and no longer than 40 min. Next, 16.69 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.075 mol) was added under atmospheric conditions. The reaction mixture was stirred for 15 h. The solvent was removed under evaporation and filtered over silica in dichloromethane. The residue was purified with column chromatography with dichloromethane as eluent. The product was obtained by crystallization in pentane (2.5 g, 12%). ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: −2.59 (s, 2H), 1.66 (s, 18H), 1.67 (s, 9H), 4.16 (s, 3H), 7.79 (d, ^3J = 8.3 Hz, 4H), 7.80 (d, ^3J = 8.3 Hz, 2H), 8.20 (d, ^3J = 8.3 Hz, 4H), 8.22 (d, ^3J = 8.3 Hz, 2H), 8.41 (d, ^3J = 8.3 Hz, 2H), 8.51 (d, ^3J = 8.3 Hz, 2H), 8.88 (d, ^3J = 4.9 Hz, 2H), 8.98 (s, 4H), 9.01 (d, ^3J = 4.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 31.61, 34.81, 52.33, 118.24, 120.56, 120.84, 123.67, 127.94, 129.52, 131.14, 134.52, 134.72, 139.14, 139.21, 147.35, 150.63, 167.48. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 710, 733, 799, 965, 1108, 1189, 1220, 1270, 1351, 1397, 1475, 1606, 1725, 2868, 2903, 2957, 3316. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 418 (5.69), 516 (4.67), 553 (4.43), 592 (4.19), 647 nm (4.15). Anal. Calcd for $C_{58}H_{56}N_4O_2 \cdot H_2O$ (M_r = 859.11): C, 81.09; H, 6.80; N, 6.52. Found: C, 81.49; H, 6.88; N, 6.36.

[5-(*p*-Carboxymethyphenyl)-10,15,20-(*p*-*tert*-butyltriphenyl)porphyrinato]tin(IV) (9a). To a solution of 1 g of **8** (1.1 mmol) in 500 mL of acetic acid was added 2.6 g of $SnCl_2$ (10 mmol), and the mixture was heated to reflux over a period of 15 h. The complete insertion of the tin was observed with TLC. The reaction was nearly quantitative. The solvent was removed on a rotary evaporator. The residue was purified with column chromatography with a mixture of dichloromethane/ethyl acetate (4:1) as eluent. The solution was concentrated on a rotary evaporator and washed three times with 10% hydrochloric acid to obtain the dichloro complex. The product was obtained by crystallization in pentane (1.1 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: 1.67 (s, 27H), 4.16 (s, 3H), 7.86 (d, ^3J = 8,3 Hz, 4H), 8.28 (d, ^3J = 8.3 Hz, 4H), 8.46 (d, ^3J = 8.3 Hz, 2H), 8.55 (d, ^3J = 8.3 Hz, 2H), 9.16 (d, ^3J = 4.9 Hz, 2H), 9.28 (s, 4H), 9.31 (d, ^3J = 4.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 31.60, 34.97, 52.49, 119.24, 121.67, 121.93, 124.10, 128.30, 130.39, 131.92, 132.87, 132.96, 133.21, 134.89, 134.98, 137.58, 145.51, 145.69, 146.52, 146.61, 146.77, 151.63, 167.23. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 741, 764, 799, 1073, 1011, 1108, 1208, 1239, 1274, 1363, 1397, 1463, 1610, 1725, 2926, 2957. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 323 (4.37), 408 (4.65), 429 (5.66), 562 (4.34), 604 nm (4.31). Anal. Calcd for $C_{58}H_{54}Cl_2N_4O_2Sn \cdot H_2O \cdot CH_2Cl_2 \cdot CH_3COOH$ (M_r = 1193.83): C, 61.37; H, 6.75; N, 4.69. Found: C, 61.30; H, 6.46; N, 4.42.

{(5-Amido-*N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-isophthalamidophenyl)-10,15,20-(*p*-*tert*-butyltriphenyl)porphyrinato}-tin(IV) (2a). To a solution of 1 g of 9a (0.97 mmol) in 300 mL of ethanol was added an excess of sodium hydroxide, and the mixture was heated to reflux over a period of 8 h to get the free carboxylic acid 9b. The completion of the reaction was monitored via TLC. The solvent was removed on a rotary evaporator, and the residue was dissolved in dichloromethane. The solution was washed three times with citric acid to protonate the carboxylic acid. The organic phase was dried with $MgSO_4$ and the solvent was removed on a rotary evaporator. The deprotection of the methyl ester is quantitative. The

deprotected tin porphyrin was dissolved in 200 mL of dichloromethane at 0 °C. A 560 mg amount of EDC (2.91 mmol), 400 mg of HOBT (2.91 mmol), and 355 mg of DMAP (2.91 mmol) were added, and the solution was stirred for 1 h at 0 °C. After that period, 600 mg of 5-amino-*N*,*N*′-bis[6-(3,3-dimethylbutyrylamino)pyridine-2-yl]isophthalamide (7) (1.1 mmol) was added to the solution and the mixture was stirred at RT for 48 h. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography on silica gel with a mixture of dichloromethane/ethyl acetate (3:1) as eluent. The product was obtained by crystallization in pentane. The yield was 300 mg (18%). ^{1}H NMR (THF-d_8, 400 MHz, RT) [δ (ppm)]: 1.09 (s, 18H), 1.66 (s, 27H), 2.26 (s, 4H), 3.41 (d, ^3J = 8.3 Hz, 2H), 6.39 (dd, ^3J = 8.0 Hz, 2H), 6.65 (dd, ^3J = 8.0 Hz, 2H), 7.04 (d, ^3J = 8.3 Hz, 2H), 7.78 (dd, ^3J = 8.0 Hz, 2H), 7.91 (d, ^3J = 8.3 Hz, 6H), 8.08 (d, ^3J = 8.0 Hz, 2H), 8.13 (m, 8H), 8.28 (d, ^3J = 8.3 Hz, 2H), 8.33 (s, 1H), 8.46 (d, ^3J = 8.3 Hz, 2H), 8.86 (s, 2H), 9.07 (d, ^3J = 4.9 Hz, 2H), 9.16 (m, 6H), 9.21 (s, 2H), 9.63 (s, 2H), 10.29 (s, 1H). ^{13}C NMR (THF-d_8, 100.5 MHz, RT) [δ (ppm)]: 29.98, 31.61, 31.83, 35.54, 50.66, 107.17, 110.00, 110.34, 118.67, 121.34, 122.30, 123.21, 123.28, 123.44, 124.28, 124.84, 124.91, 127.08, 133.23, 133.99, 134.04, 134.29, 135.60, 135.80, 136.87, 138.60, 140.67, 141.41, 144.95, 147.95, 148.47, 148.63, 151.33, 151.87, 152.32, 165.49, 166.69, 171.01. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 741, 799, 1011, 1031, 1108, 1239, 1393, 1447, 1513, 1586, 1679, 2868, 2907, 2957, 3312. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 305 (4.33), 406 (4.34), 427 (5.43), 560 (4.01), 601 (3.92). Anal. Calcd for $C_{99}H_{95}N_{17}O_7Sn{\cdot}2CDCl_3$ (M_r = 1994.4): C, 60.82; H, 5.00; N, 11.75. Found: C, 60.36; H, 5.19; N, 11.64.

5-(*p*-*tert*-Butylacetatophenoxy)-10,15,20-(*p*-*tert*-butyltriphenyl)-porphyrin (10). A solution of 6.8 mL of pyrrole (0.10 mol), 12.56 mL of 4-*tert*-butylbenzaldehyde (0.075 mol), 5.90 g of *tert*-butyl 2-(4-formyl-phenoxy)acetate (0.025 mol), 20 mL of ethanol, and 100 mg of tetraphenylphosphonium chloride in 2.5 L of dichloromethane was stirred for 30 min. Then 6.3 mL of boron trifluoride etherate (0.049 mol) was added changing the color of the solution to purple red. The mixture was stirred for at least 35 min and no longer than 40 min. Then 16.69 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.075 mol) was added under open air conditions. The reaction mixture was stirred for 15 h. The solvent was removed under evaporation and filtered over silica in dichloromethane. The residue was purified with column chromatography with dichloromethane as eluent. The product was obtained by crystallization in pentane. The yield was 2.7 g (11.8%). ^{1}H NMR ($CDCl_3$,400 MHz, RT) [δ (ppm)]: −2.65 (s, 2H), 1.66 (m, 36H), 4.86 (s, 2H), 7.33 (d, ^3J = 8.3 Hz), 7.79 (d, ^3J = 8.1 Hz), 8.20 (m, 8H), 8.94 (m, 8H). ^{13}C NMR ($CDCl_3$,100.5 MHz, RT) [δ (ppm)]: 28.11, 31.63, 34.83, 66.02, 82.56, 112.92, 119.42, 120.25, 123.64, 131.04, 134.54, 134.58, 135.64, 135.68, 139.28, 150.53, 157.68, 168.3. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 729, 799, 965, 1235, 1297, 1444, 1505, 1586, 1675, 2868, 2926, 2957, 3312. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 418 (5.69), 516 (4.22), 552 (3.99), 591 (3.59), 648 (3.69). Anal. Calcd for $C_{62}H_{64}N_4O_3{\cdot}CH_2Cl_2$ (M_r = 998.13): C, 75.81; H, 6.66; N, 5.61. Found: C, 75.63; H, 6.64; N, 5.47.

5-(3,5-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]isophthalamideamidoacetatophenoxy)-10,15,20-(*p*-*tert*-butyltriphenyl)porphyrin (2b). A solution of 1 g of 10 (1.1 mmol) and 200 mL of formic acid was stirred for 4 h to obtain the deprotected acid 11. The completed reaction was observed via TLC. After that period the solvent was removed on a rotary evaporator and the product was dried on an oil pump. The dried product was dissolved in dichloromethane at 0 °C. A 210 mg amount of EDC (1.1 mmol), 150 mg of HOBT (1.1 mmol), and 135 mg of DMAP (1.1 mmol) were added, and the solution was stirred for 1 h at 0 °C. After that period, 600 mg of 5-amino-*N*,*N*′-bis-[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]isophthalamide (7) (1.1 mmol) was added to the solution and the mixture was stirred at room temperature for 48 h. The solvent was removed on a rotary evaporator, and the residue was purified with column chromatography on silica gel with a mixture of dichloromethane/ethyl acetate (3:1) as eluent. The product was obtained by crystallization in pentane. The yield was 460 mg (30%). ^{1}H NMR ($CDCl_3$, 400 MHz, RT) [δ (ppm)]: −2.69 (s, 2H), 1.18 (s, 18H), 1.57 (s, 18H), 1.62 (s, 9H), 2.45 (s, 4H), 5.01 (s, 2H), 7.37 (d, ^3J = 8.5 Hz, 2H), 7.67 (d, ^3J = 8.5 Hz, 2H), 7.74 (d, ^3J = 8.5 Hz, 2H), 8.00 (t, ^3J = 8.0 Hz, 2H), 8.08 (d, ^3J = 8.5 Hz, 2H), 8.14 (d, ^3J = 7.3 Hz, 2H), 8.20 (d, ^3J = 7.3 Hz, 2H), 8.65 (s, 1H), 8.68 (s, 2H), 8.82 (d, ^3J = 4.6 Hz), 8.90 (m, 10H), 9.39 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.5 MHz, RT) [δ (ppm)]: 29.78, 31.40, 31.54, 31.58, 34.73, 34.78, 50.95, 68.43, 109.64, 110.70, 113.15, 118.58, 119.73, 120.34, 120.47, 122.31, 123.57, 131.37, 134.47, 135.47, 135.97, 138.24, 139.09, 139.16, 149.06, 150.30, 150.50, 156.54, 163.77, 167.91, 171.68. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 729, 799, 965, 984, 1235, 1297, 1444, 1505, 1586, 1675, 2868, 2926, 2957, 3312. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 301 (4.32), 400 (4.52), 419 (5.30), 517 (3.90), 553 (3.68), 593 (3.42), 648 (3.48). Anal. Calcd for $C_{88}H_{91}N_{11}O_6$·ethyl acetate (M_r = 1486.84): C, 74.32; H, 6.71; N, 10.36. Found: C, 74.04; H, 7.08; N, 10.03.

[5-(3,5-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]isophthalamideamidoacetatophenoxy)-10,15,20-(*p*-*tert*-butyltriphenyl)porphyrinato]tin(IV) (2c). A 200 mg amount of 2b (0.15 mmol) was dissolved in 100 mL of acetic acid. A 500 mg amount of $SnCl_2$ (1.8 mmol) was added to this solution, and the mixture was heated to reflux over a period of 15 h. The complete insertion of the tin was observed with TLC. The reaction was nearly quantitive. The solvent was removed on a rotary evaporator. The residue was purified with column chromatography with a mixture of dichloromethane/methanol (9:1) as eluent. The solution was concentrated on a rotary evaporator, and the product was obtained by crystallization in pentane. The yield was 231 mg (97%). ^{1}H NMR (THF-d_8, 400 MHz, RT) [δ (ppm)]: 1.08 (s, 18H), 1.63 (s, 27H), 2.25 (s, 4H), 4.62 (s, 2H), 7.39 (d, ^3J = 8.5 Hz, 2H), 7.75 (t, ^3J = 8.0 Hz, 2H), 7.89 (d, ^3J = 8.3 Hz, 6H), 8.03 (d, ^3J = 7.8 Hz, 2H), 8.08 (d, ^3J = 7.8 Hz, 2H), 8.22 (d, ^3J = 8.3 Hz, 6H), 8.25 (d, ^3J = 8.5 Hz, 2H), 8.41 (s, 1H), 9.12 (m, 10H), 9.37 (s, 2H), 9.50 (s, 2H), 9.67 (s, 1H). ^{13}C NMR (THF-d_8, 100.5 MHz, RT) [δ (ppm)]: 30.00, 31.63, 31.87, 35.83, 50.67, 68.15, 109.98, 110.34, 111.89, 122.20, 122.31, 122.49, 124.66, 131.62, 133.03, 135.55, 136.54, 136.80, 139.31, 140.67, 147.78, 151.37, 151.96, 152.18, 154.07, 159.41, 165.37, 167.98, 171.00. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 718, 799, 1011, 1031, 1235, 1297, 1363, 1397, 1447, 1505, 1586, 2864, 2961. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 305 (4.25), 406 (4.19), 427 (5.33), 560 (3.91), 601 nm (3.83).

[5-(3,5-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]isophthalamideamidoacetatophenoxy)-10,15,20-(*p*-*tert*-butyl-triphenyl)porphyrinato]zinc (2d). A 400 mg amount of 2b (0.29 mmol) was dissolved in THF, and 160 mg of zinc acetate (0.86 mmol) was added. The mixture was heated to reflux over a period of 4 h. The metal insertion was nearly quantitative. The solvent was removed on a rotary evaporator, and the residue was purified with column chromatography on silica gel with a mixture of dichloromethane/ethyl acetate (3:1) as eluent. Final crystallization in pentane gave a purple red solid in good yield (410 mg, 98%). ^{1}H NMR (THF-d_8, 400 MHz, RT) [δ (ppm)]: 1.10 (s, 18H), 1.62 (s, 27H), 2.28 (s, 4H), 5.03 (s, 2H), 7.50 (d, ^3J = 8.5 Hz, 2H), 7.75 (dd, ^3J = 8.0 Hz, 2H), 7.80 (d, ^3J = 8.3 Hz, 6H), 8.04 (d, ^3J = 7.8 Hz, 2H), 8.08 (d, ^3J = 7.8 Hz, 2H), 8.14 (d, ^3J = 8.3 Hz, 6H), 8.19 (d, ^3J = 8.5 Hz, 2H), 8.31 (s, 1H), 8.71 (d, ^3J = 1.5 Hz, 2H), 8.87 (m, 8H), 9.29 (s, 2H), 9.66 (s, 2H), 10.01 (s, 1H). ^{13}C NMR (THF-d_8, 100.5 MHz, RT) [δ (ppm)]: 30.01, 31.66, 31.94, 35.41, 50.70, 68.99, 109.98, 110.33, 113.72, 120.71, 121.50, 122.75, 122.87, 124.13, 131.39, 132.25, 135.37, 136.49, 136.93, 138.12, 140.4, 140.68, 141.64, 150.83, 151.16, 151.42, 151.97, 158.63, 165.46, 168.24, 171.04. FT-IR (diamond, RT) [$\tilde{\nu}$ (cm^{-1})]: 718, 795, 995, 1069, 1227, 1297, 1444, 1505, 1583, 1675, 2868, 2903, 2953, 3277, 3397. UV/vis (CH_2Cl_2) [λ_{max}, nm (log ϵ)]: 303 (4.34), 399 (4.16), 421 (5.19), 549 (3.85), 593 (3.50). Anal. Calcd for $C_{88}H_{89}N_{11}O_6Zn{\cdot}0.66CH_2Cl_2$ (M_r = 1518): C, 70.12; H, 6.00; N, 10.14. Found: C, 70.60; H, 5.91; N, 9.76.

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Supporting Information Available: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of Sn porphyrin and time−absorption profile, reflecting the formation and decay of the singlet excited state. This material is available free of charge via the Internet at http://pubs.acs.org.

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