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- Authors: Max von Delius, Youzhi Xu, Bingzhe Wang, Ramandeep Kaur, Martin Minameyer, Michael Bothe, thomas drewello, and Dirk Guldi

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A Supramolecular [10]CPP Junction Enables Efficient Electron Transfer in Modular Porphyrin-[10]CPP – Fullerene Complexes

Youzhi Xu,^{*a*,‡} Bingzhe Wang,^{*b*,‡} Ramandeep Kaur,^{*b*} Martin B. Minameyer,^{*b*} Michael Bothe,^{*a*} Thomas Drewello,^{*b*} Dirk M. Guldi,^{*b**} Max von Delius^{*a**}

Abstract: [10]Cycloparaphenylene ([10]CPP) has recently been shown to be an excellent supramolecular receptor for C_{60} and C_{70} . Here we report efficient photoinduced electron transfer across a [10]CPP moiety that serves as a modular, yet rigid, non-covalent bridge between a zinc porphyrin and a diverse range of fullerenes. The first preparation of iodo-[10]CPP is the cornerstone of our synthesis of a porphyrin-[10]CPP conjugate, which was found to bind C_{60} , C_{70} , $(C_{60})_2$ and other fullerenes with association constants beyond $10^5\ M^{\text{-1}}.$ Fluorescence and pump-probe spectroscopy revealed intramolecular energy transfer between CPP and porphyrin, as well as efficient charge separation between porphyrin and fullerenes, affording up to 0.5 μ s lived charge-separated states. The advantage of our modular approach towards electron donor-acceptor dyads is particularly evident in the case of dumbbell-shaped (C₆₀)₂, which gave rise to intricate charge transfer behaviour in unusual 1:1 and 2:1 complexes. In a broader context, our results suggest that [10]CPP and its cross-coupled derivatives could act as supramolecular mediators of charge transport in organic electronic devices.

Following the first synthesis of a cycloparaphenylene (CPP) in 2008,¹ this compound class has been developed² and diversified³ at a remarkable pace. Recently, even the synthesis of an elusive "nanobelt" was achieved,⁴ indicating that strained aromatic macrocycles can now be prepared that were previously considered beyond the reach of organic synthesis. Recent work on the gas-phase identification of CPP catenanes and the observation of "russian doll" CPP \supset CPP complexes suggests that "nanohoops" offer rich opportunities in supramolecular chemistry.⁵ [10]CPP is arguably the most interesting family member in this respect, because it has been shown to exhibit the perfect ring size for a strong convex-concave π - π interaction with C₆₀,⁶ which raises the intriguing question whether [10]CPP could play a role as an additive in organic electronic devices.⁷

With the exception of one report on the formation of charge transfer complex [10]CPP⁺ \supset C₆₀⁻ under extremely high pressure

[a]	Y. Xu, M. Bothe, Prof. Dr. M. von Delius
	Institute of Organic Chemistry and Advanced Materials
	University of Ulm
	Albert-Einstein-Allee 11, Ulm 89081, Germany
	E-mail: max.vondelius@uni-ulm.de
[b]	B, Wang, R. Kaur, M. B. Minameyer, Prof. Dr. T. Drewello, Prof. Dr.
	D. M. Guldi
	Department of Chemistry and Pharmacy & Interdisciplinary Center
	for Molecular Materials
	Friedrich-Alexander University Erlangen-Nürnberg
	Egerlandstrasse 3, Erlangen 91058, Germany
	E-mail: dirk.guldi@fau.de
[‡]	These authors contributed equally.
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(6 GPa),⁸ the charge transport properties of [10]CPP⊃fullerene inclusion complexes⁹ are unexplored, which is in part due to the lack of precursors that would allow the general functionalization of [10]CPP by cross-coupling reactions. Itami has reported the synthesis of chloro-[10]CPP, along with its Ni-catalyzed homocoupling into ([10]CPP)₂,¹⁰ but the synthesis of more reactive and versatile iodinated or brominated [10]CPP substrates for cross-coupling reactions remains an unsolved problem.

Herein, we report the first synthesis of iodo-[10]CPP, based on a late-stage *ipso* substitution strategy (TMS \rightarrow I). Starting from iodo-[10]CPP, we were able to carry out a highly efficient Sonogashira cross-coupling to afford conjugate 1, in which [10]CPP (Figure 1, red) is covalently linked to a prototypical electron donor dye (zinc porphyrin, blue). This compound can be transformed into supramolecular inclusion complexes (1-fullerene), which feature a well-defined spatial separation of electron donor and acceptor, by the simple addition of equimolar amounts of pristine fullerenes. This modularity is a unique advantage compared to previous studies on conventional porphyrin-fullerene conjugates,11 as well as supramolecular complexes that are based on both functionalized porphyrins and fullerenes.12



Figure 1. Structure of supramolecular electron donor-acceptor complex 1⊃PCBM and schematic illustration of photoinduced electron transfer.

The synthesis of a [10]CPP derivative bearing a functional group that would allow mild and efficient cross-coupling reactions marked the start of this study. To our disappointment, we were unable to transform [10]CPP directly into bromo- or iodo-[10]CPP, which is in agreement with a recent study on the bromination of highly strained [n]CPPs (n ≤ 8).¹³ Hence, we decided to use a trimethylsilyl (TMS) group as a functional handle that would allow the late-stage introduction of an iodo substituent.

As shown in Scheme 1a, our successful synthesis of iodo-[10]CPP follows Jasti's reported synthesis of [10]CPP,¹⁴ with some crucial deviations, such as the use of a methoxymethyl protecting group (MOM) in the sixth step of the sequence (2, Scheme 1a). In a Suzuki-Miyaura reaction, aryl dibromide 3 was

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coupled with aryl diboronic ester 4^{3c} and a subsequent reductive aromatization furnished TMS-[10]CPP in acceptable 10% yield over the challenging final two steps. Using iodine monochloride (ICI), we were able to convert TMS-[10]CPP into iodo-[10]CPP, and a copper-free Sonogashira reaction furnished conjugate **1** in quantitative yield. A qualitative ¹H NMR titration provided evidence for selective binding of C₆₀ to the CPP ring, but not the porphyrin (Scheme 1, bottom).

Scheme 1.a,b



^a Reaction conditions: (i) imidazole, TMSCI, DCM, 0 $^{\circ}$ C \rightarrow RT; (ii) *n*-BuLi, TMSCI, THF, -78 $^{\circ}$ C, 95% (two steps); (iii) 2% HCI, DCM, MeOH, 99%; (iv) PhI(OAc)₂, MeOH, 0 $^{\circ}$ C; (v) 1,4-diiodobenzene, *n*-BuLi, THF, -78 $^{\circ}$ C, MeOH, 78%; (vi) NaH, MOM-CI, THF, -60 \rightarrow -40 $^{\circ}$ C, 90%; (vii) 1,4-dibromobenzene, *n*-BuLi, THF, -78 $^{\circ}$ C, CH₃I, DMF, 85%; (viii) *n*-BuLi, THF, -120 $^{\circ}$ C, CH₃I, DMF, 62%; (ix) Pd(OAc)₂, Cs₂CO₃, DMF, *i*-PrOH, 100 $^{\circ}$ C; (x) sodium naphthalenide, -78 $^{\circ}$ C, 10% (two steps); (xi) ICI, -78 $^{\circ}$ C \rightarrow -20 $^{\circ}$ C, 82%; (xii) Pd(Ph₃P)₄, Et₃N, DMF, RT \rightarrow 40 $^{\circ}$ C, quant. Ar: 4-tert-butyl-phenyl. ^b Partial ¹H NMR spectra (CDCI₃, 298K, 400 MHz).

With compound **1** in hand, we proceeded to explore its physicochemical properties. In the ground state, the typical Soretband and Q-band absorptions of the porphyrin evolve at 425 and 551 / 591 nm, while absorptions of [10]CPP are discernable around 340 nm (Figure S1). As shown in the 3D fluorescence spectrum (Figure 2), the excited state of conjugate **1** is dominated by an intramolecular energy transfer from the energy donating [10]CPP to the energy accepting porphyrin.¹⁵



Figure 2. Room temperature 3D fluorescence spectrum of porphyrin-[10]CPP conjugate **1** upon 300 to 450 nm excitation in toluene and schematic illustration of energy transfer. For a porphyrin reference see Figure S2.

To gain insight into the formation of 1⊃fullerene electron donoracceptor complexes, we turned to C₆₀, C₇₀, azafullerene derivative C₅₉N-DPS, C₆₀ derivate PCBM and the fullerene dimer (C₆₀)₂ and conducted fluorescence titrations in toluene.^{6,16-20} The intensity of the porphyrin-centered fluorescence, with maxima at 600 and 650 nm, was found to decrease exponentially with increasing fullerene concentrations. Reaching the endpoint in the titrations the fluorescence intensity quenched to 18.6%, 18.4%, 19.5%, 30.0% and 13.0% for C₆₀, C₇₀, C₅₉N-DPS, PCBM and (C₆₀)₂, respectively. As such, the fluorescence intensities are in sound agreement with the electron acceptor strength of the fullerene, that is, C₅₉N-DPS > C₆₀, C₇₀ > PCBM.²¹

From fitting the data, we derived the association constants for the supramolecular electron donor-acceptor complexes (Figure 3, Figures S14-S18). A remarkably high association constant of (1.6 ± 0.1) × 10⁶ M⁻¹ was found for the one-step binding of C₆₀, while $(C_{60})_2$ is subject to two consecutive steps with underlying association constants of (4.7±0.1) \times 10⁶ and (1.9±0.05) \times 10⁶ M⁻ ^{1,22} For C₇₀ and (aza)fullerene monoadducts PCBM and C₅₉N-DPS, the association constant is ca. one order of magnitude lower. These results suggest that for this set of fullerenes the relative binding affinities are mainly governed by the three-dimensional shape of the guest molecule (e.g., C₆₀ is the only guest that can rotate freely within [10]CPP in all three dimensions). Independent support for the notion of strong fullerene binding was provided by electrospray ionization (ESI) mass spectrometry, including unprecedented MS/MS measurements of such complexes (Figures S11-S12).

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Figure 3. Structures of electron acceptors C₆₀, C₇₀, PCBM, C₅₉N-DPS and (C₆₀)₂, their association constants (*K*_A) with conjugate **1** and lifetimes (τ) of the corresponding charge-separated states.



Figure 4. (a) Differential absorption spectra obtained by femtosecond pump probe experiments (430 nm / 500 nJ) of representative complex $1 \supset C_{60}$ ($C_{(1)} = 1 \times 10^{-5}$ M; $C(C_{60}) = 1 \times 10^{-4}$ M) in benzonitrile with time delays of 2, 5, and 240 ps correlating with the absorption spectra of the porphyrin second singlet excited state, the porphyrin first singlet excited state, and the charge separated state, respectively, at room temperature. The insert shows the zoom in image between 900 to 1200 nm. (b) Time-absorption profiles and corresponding fits of the characteristic absorption fingerprints of the C_{60} radical anion at 1090 nm (black) and the porphyrin radical cation at 670 nm (red) to illustrate the internal

conversion, the charge separation, and the charge recombination. 3D plots are provided in Figure S19.

The nature of the singlet excited-state deactivation in 1-fullerene complexes, that is, charge separation and charge recombination, was corroborated by means of time-resolved transient absorption spectroscopy. 430 nm was chosen to excite the porphyrin in 1 and in the 1-fullerene complexes exclusively despite a 10-fold excess of the fullerene in the latter case. In reference experiments with 1, the porphyrin (second) singlet excited state features with its characteristic 630, 750 and 900 nm transient was seen to internally convert into the (first) singlet excited state and to intersystem cross with to afford the triplet excited state; Transient features include 500 and 850 nm fingerprints, respectively. Figure 4 documents in the case of $1 \supset C_{60}$ the prompt detection of only the same porphyrin (second) singlet excited state features - vide supra - and attests to its exclusive excitation. Following internal conversion, a fast decay of the porphyrin (first) singlet excited state goes hand-in-hand with the growth of maxima in the visible range at 530, 580, 620, and 660 nm as well as in the near-IR range at 1090 nm. The earlier maxima match the fingerprint absorptions of the one-electron oxidized form of the porphyrin,23 while the latter maximum is the known marker of the one-electron reduced form of C₆₀.²⁴

Photoexcitation of $1 \supset C_{60}$ is followed by the formation of a metastable $1^{++} \supset C_{60}^{--}$ charge-separated state. Figures 4 and S21 document that in femto- and nanosecond pump-probe experiments, respectively, the charge-separated state decays in benzonitirile via the direct recovery of the ground state. Lowering the solvent-related stabilization of the $1^{++} \supset C_{60}^{--}$ charge-separated state in, for example, toluene shifts its energy above that of the C_{60} triplet excited state. As such, the 750 nm fingerprint absorption as seen in reference experiments with C_{60} in Figure S25 evolves as a product of charge recombination.²⁵ It is then the latter that reinstates slowly the ground state. Similarly, we detected in $1 \supset$ fullerene the fingerprint absorptions of the well-known values of one-electron reduced forms for C_{70} at 1380 nm,²⁶ for C_{59} N-DPS at 1050 nm,²⁷ and for PCBM at 1040 nm.²⁸

The case of $(C_{60})_2$ is particularly interesting because, depending on stoichiometry and concentration, different molar ratios of a 1:1 $(1 \supset (C_{60})_2)$ and 2:1 $(1 \supset (C_{60})_2 \supset 1)$ complex are present in solution. Common to both is the one-electron oxidized form of the porphyrin with maxima in the visible range at 530, 580, 620, and 660 nm as well as the one-electron reduced form of (C₆₀)₂ in the near-IR range at 1050 nm. As illustrated in Figure 5, the charge separation and recombination kinetics differed, however, significantly from what has been seen for C₆₀, C₇₀, C₅₉-DPS, and C₆₀-PCBM – vide supra. For example, in $1 \supset (C_{60})_2$ the desymmetrization of the C₆₀ moieties results in two distinct charge recombination processes, that is a rapid one (Figure 5a) with a lifetime of 2.5±0.4 ns and a slow one (Figure 5b) with a lifetime of 13.4±2.3 ns involving the proximal and distant fullerene cores, respectively. Notably, the latter is longer-lived than any other 1 monofullerene charge-separated state that we observed in this study.

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Figure 5. Schematic illustration of the charge recombination processes (blue arrows) observed in (a, b) $1^{++} \supset (C_{60})_2$. and (c) $1^{++} \supset (C_{60})_2$. -1.

Only one electron recombination process was observed in the more symmetric 2:1 complex $(1 \supset (C_{60})_2 \subset 1$, Figure 5c). However, by virtue of charge delocalization in the porphyrin⁺⁺- [10]CPP \supset ($C_{60})_2$, \subset [10]CPP-porphyrin charge-separated state, and in stark contrast to the 1⁺⁺ \supset C₆₀⁻⁻ system, a lifetime of up to 541.8±112.8 ns was observed,²⁹ which is among the longest-lived charge-separated states in fullerene / porphyrin containing electron donor-acceptor systems.³⁰ This first study of *intra*(supra)molecular electron transfer to (C_{60})₂,³¹ attests to the unique potential of our modular, non-covalent approach. Nevertheless, it should be noted that, despite the conformational rigidity of our entire system and the high association constants, our results reflect average values, particularly in respect to fullerene rotation and translation ("shuttling" of (C_{60})₂)^{31a} within the CPP host.

In conclusion, we have successfully carried out the synthesis of a porphyrin-[10]CPP conjugate and studied its strong association with a range of fullerenes. Pump probe spectroscopy demonstrated that [10]CPP as a supramolecular junction enables efficient charge transport between a porphyrin electron donor and unmodified fullerene electron acceptors. These results, together with Yamago's recent report on the thin-film conductivity of [10]CPP and its alkoxy derivatives,³² imply that supramolecular complexes of [10]CPP and fullerenes may be a useful addition to the toolbox of organic electronics.³³

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Modular dyads: The successful synthesis of iodo-[10]CPP allowed the study of photoinduced electron transfer in unusual supramolecular porphyrin-[10]CPP⊃fullerene complexes. Youzhi Xu, Bingzhe Wang, Ramandeep Kaur, Martin B. Minameyer, Michael Bothe, Thomas Drewello, Dirk M. Guldi,* Max von Delius*

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A Supramolecular [10]CPP Junction Enables Efficient Electron Transfer in Modular Porphyrin-[10]CPP⊃Fullerene Complexes