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Synthesis and fluorescence properties of a porphyrin–fullerene molecular wire†

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ABSTRACT: The synthesis and photophysical studies of a butadiyne-linked porphyrin–C_{60} dyad (ZnP–C_{60}) **6** are described. This is the first porphyrin–[60]fullerene dyad in which the two chromophores are conjugatively linked through a 'molecular wire'. The UV–visible absorption spectrum for dyad **6** is slightly red shifted relative to the porphyrin precursor **5** whose fluorescence is all but quenched by the attached C_{60}. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: molecular wire; fullerene; porphyrin; electron transfer; fluorescence quenching

INTRODUCTION

The unique chemical and photophysical properties of [60]fullerene (C_{60}) have generated considerable interest in its role as a highly efficient electron acceptor in covalent donor–acceptor systems,[1] with potential applications in photovoltaic devices and artificial photosynthetic complexes,[2] solar energy conversion[3] and biological applications such as photodynamic therapy.[4] The underlying factors responsible for these properties include the high degree of symmetry on the fullerene sphere and in the arrangement of its molecular orbitals.[5,6] C_{60} is able to accept up to six electrons reversibly because of triply degenerate low-lying LUMOs located $\sim$1.8 eV above the HOMO.[1b,5] The irradiation of C_{60} creates a short-lived C_{60} singlet ($^1C_{60}$*) that rapidly and efficiently generates the C_{60} triplet ($^3C_{60}$*) via intersystem crossing.[6] In turn, the long-lived C_{60} triplet can sensitize the formation of highly reactive singlet molecular oxygen ($^1O_2$) via energy transfer to ground state dioxygen.[7]

It is widely accepted that C_{60} is an ideal electron acceptor in donor–acceptor (D–A) systems designed to mimic the photosynthetic reaction center (PRC).[3] The long-lived charge-separated (CS) states observed in fullerene systems can be attributed to the low reorganization energy of the fullerene[8] and the suppression of back electron transfer (BET) events by forcing charge recombination (CR) into the Marcus inverted region.[9] Such systems exhibit very rapid photoinduced electron transfer (ET), affording the CS state with high quantum yield when the distance between the donor and acceptor chromophores is small. Systems designed to mimic the PRC must exhibit a preference for ET over energy transfer (EN) at longer distances, since the EN rate decreases rapidly with increasing distance between the chromophores.[1,2,8]

A promising strategy to facilitate ET over long distances involves the incorporation of a 'molecular wire' in the D–A system.[10] Recent studies of long-range charge separation (CS) in D–A systems have shown that linear π-conjugated polyene and polyyne spacers dramatically enhance through-bond electronic coupling between donors and acceptors.[11] Systems in which redox centers are separated by 'molecular wires', such as polyenes and polyynes, exhibit efficient, long-range ET and EN. Although the distance between the donor and acceptor is an important consideration when investigating ET and EN processes, studies of these parameters as they apply to conjugated π-systems are scarce. In polyene-linked D–A systems, rotation about single bonds can lead to variations in the D–A distance and reduced conjugation within the system.[12] In contrast, a fixed distance is maintained between the chromophores in polyyne-linked systems. Thus, alkynyl groups permit enhanced conjugation in conformationally rigid D–A systems and afford geometrically well-defined materials that simplify the interpretation of physical data. Yamada *et al.* synthesized the first D–A system where a porphyrin was covalently linked to C_{60} via an alkyne bridge.[10] Although this fullerenopyrrolidine derivative lacked 'true' conjugation between the chromophores, the accelerated rate of CS over an

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analogous amide-linked system was explained in terms of the enhanced electronic coupling between the porphyrin and C_{60} moieties.

Komatsu *et al.* were the first to report the synthesis and properties of (trimethylsilyl)ethynyl- and phenylethynylhydrofullerenes, the first alkyne C_{60} derivatives.[13] These derivatives were synthesized via nucleophilic attack of the appropriate alkynyllithium reagent on the fullerene, followed by quenching of the C_{60} anion with trifluoroacetic acid. Subsequently, Diederich and coworkers examined the chemistry of a variety of fullerene–acetylene hybrids.[14] We now report the preparation of 1-ethynyl-2-methyl[60]fullerene and its direct oxidative heterocoupling to 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin, to afford the first completely conjugated butadiyne-linked porphyrin–fullerene dyad, the prototype of a new family of materials.

RESULTS AND DISCUSSION

Syntheses of fullerene derivative 2 and alkynyl-substituted porphyrin 5

The synthesis of the new alkynyl fullerene derivative **2** was modified from the procedure previously reported by Diederich and co-workers for analogous materials.[15] As shown in Scheme 1, nucleophilic addition of lithium (trimethylsilyl)acetylide to C_{60}, followed by quenching with iodomethane, furnished **1** in moderate yield. Deprotection of the alkyne with potassium carbonate, followed by purification on silica gel with cyclohexane as eluent, afforded the fullerene derivative **2**.

The synthesis of *p*-ethynyltetraaryl porphyrin **5** was carried out as shown in Scheme 2, using the one-step procedure previously reported in the literature.[16] Condensation of the mixed aldehydes with pyrrole in refluxing glacial acetic acid and nitrobenzene afforded a crude mixture of tetraaryl porphyrins including the desired porphyrin **3** as evidenced by TLC and MALDI-TOF analysis. The crude porphyrin mixture was metallated using zinc acetate dihydrate in refluxing chloroform–methanol solution (2:1), and was purified on a long silica gel column with hexane–CH_2Cl_2 (4:1) as eluent. Deprotection of **4** was accomplished by reaction with an excess of tetrabutylammonium fluoride in THF at room temperature, to afford **5** as a purple crystalline solid in near quantitative yield (95%). Zinc porphyrin **5** was fully characterized by ^1H NMR and MALDI-TOF analysis.

Synthesis of porphyrin–fullerene dyad 6 (Scheme 3)

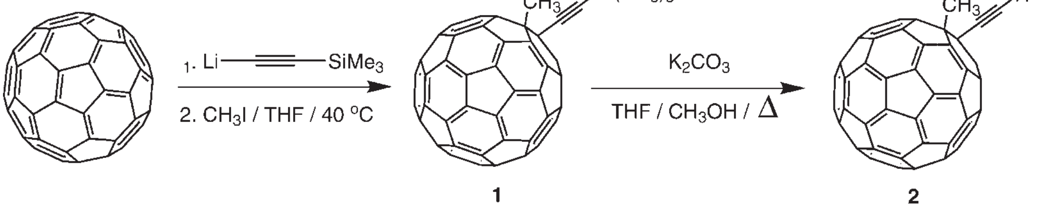
The oxidative heterocoupling of fullerene derivative **2** with zinc porphyrin **5** was adapted from a coupling procedure previously reported by Diederich *et al.*[17] Using the Hay catalyst (CuCl–TMEDA–O_2) prepared *in situ* in chlorobenzene at room temperature, a mixture of three new compounds was obtained. The non-fluorescent dyad **6** was separated from the other products by preparative TLC using cyclohexane and hexane–CH_2Cl_2 (3:1) as eluents. The remaining two products were characterized by MALDI-TOF as butadiyne-linked ZnP–ZnP and C_{60}–C_{60} dyads arising from competitive oxidative homocoupling under the reaction conditions.

UV–visible spectra of 5 and 6

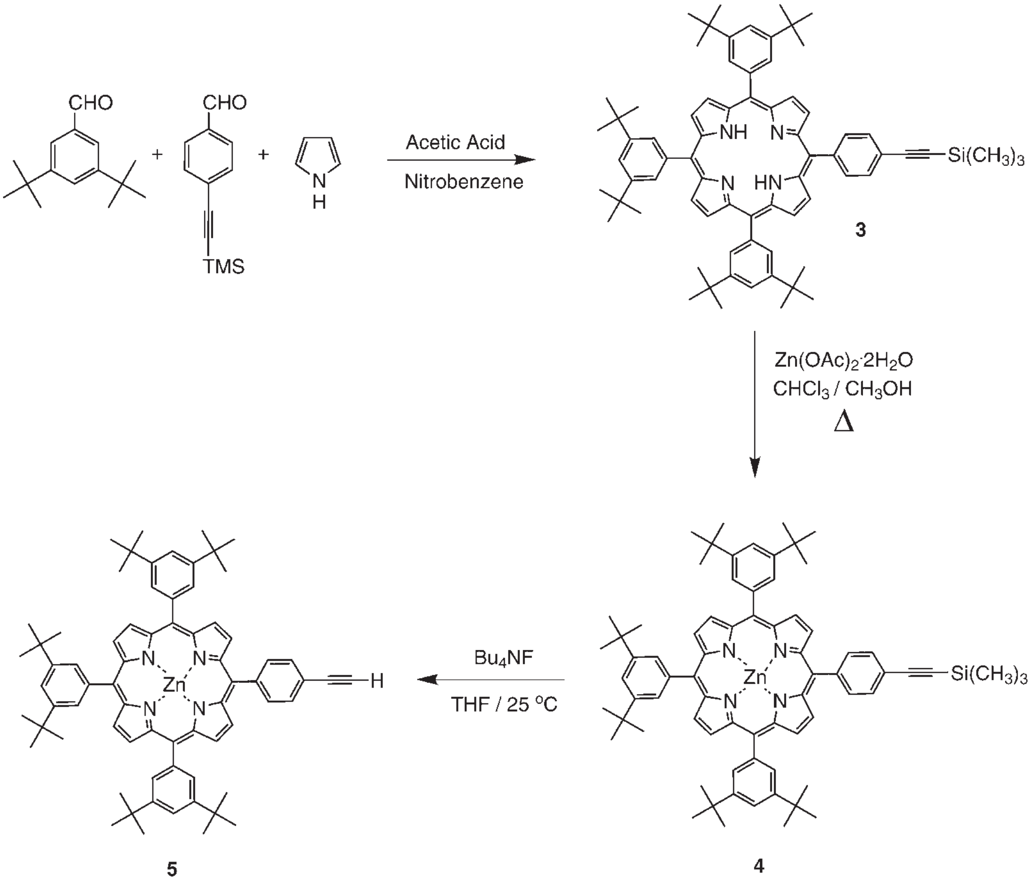
The UV–vis absorption spectra for zinc porphyrin (ZnP) **5** and dyad (ZnP–C_{60}) **6** at 10 μM concentration in chloroform are depicted in Fig. 1. The spectrum for **6** shows strong absorption bands for both the porphyrin and fullerene moieties and is consistent with the UV–visible spectra of other porphyrin–fullerene dyads.[18] Although there is a small red shift in the spectrum for Zn dyad **6** relative to precursor Zn porphyrin **5**, there is no indication of enhanced absorption of the dyad or of any ground-state electronic interaction between the chromophores.

Fluorescence and fluorescence lifetimes of 5 and 6

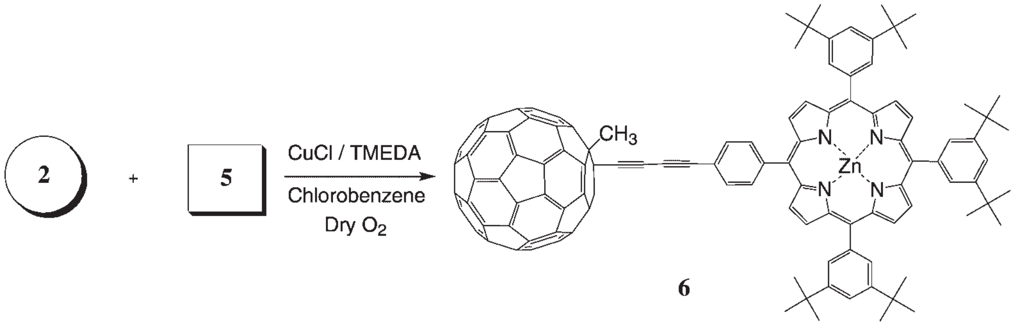
In chloroform, zinc porphyrin **5** exhibits a fluorescence maximum near 605 nm when excited at 400 nm, where most of the incident radiation is absorbed by the porphyrin and not the fullerene (see Fig. 2). The ZnP–C_{60} dyad **6,** similarly excited at 400 nm, shows a typical ZnP emission spectrum but the intensity is reduced relative to that of **5** by a factor of $>10^2$. Thus, the porphyrin fluorescence is almost entirely quenched by the attached fullerene moiety. The characteristic C_{60} fluorescence at ~700 nm is too weak to be observed on our instrument.



Scheme 1. Synthesis of 1-ethynyl-2-methyl[60]fullerene (**2**)



Scheme 2. Synthesis of zinc(II) 5-{4-(ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)}porphyrin (**5**)



Scheme 3. Synthesis of zinc(II) 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin–1-ethynyl-2-methyl[60]-fullerene dyad **6**

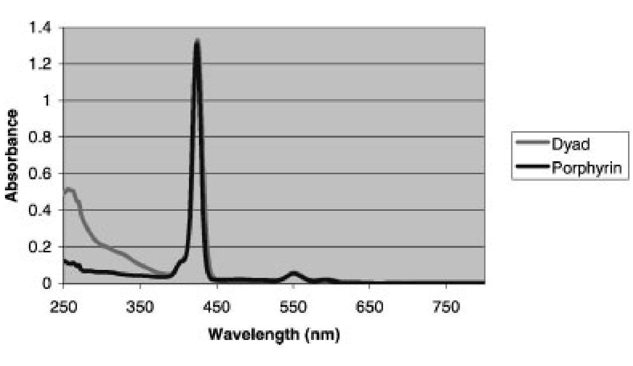


Figure 1. UV–visible absorption spectra of Zn–P **5** and Zn–P–C_{60} **6** at 10 μM concentration in chloroform

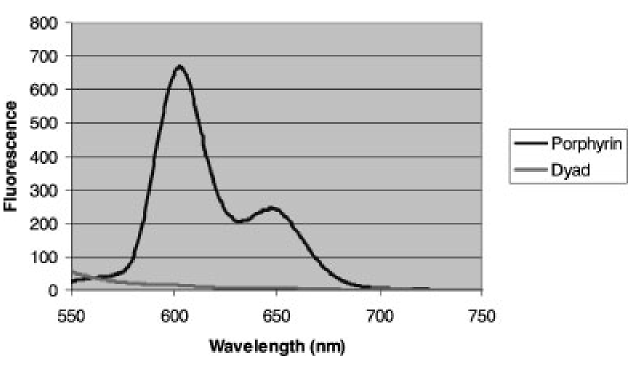


Figure 2. Fluorescence spectra of Zn–P **5** and Zn–P–C_{60} **6** at 10 μM concentration in chloroform

The fluorescence lifetime τ_f of ZnP **5** at 630 nm in chloroform was determined to be ~1.6 ns, which is in accordance with literature values for analogous zinc tetraaryl porphyrins.[19] Analysis of the fluorescence decay curve for **6** at 630 nm revealed a major component at 11 ps (99.1%) and minor components at 1.9 ns (0.8%) and 8.1 ns (0.1%). Since accurate measurement of fluorescence lifetimes on the order of 10 ps or less is beyond the limits of our instrument, we suggest that the fluorescence lifetime of ZnP–C_{60} **6** is probably less than 10 ps, indicating $\tau_0/\tau_f > 10^2$.

CONCLUSION

A new butadiyne-linked porphyrin–C_{60} dyad **6** was synthesized according to the reaction pathways presented in Schemes 1–3. The competitive homo- and heterocoupling reactions observed in the final step of the synthesis of **6** were quantitative with respect to disappearance of the starting materials. These reactions can be a useful methodology for constructing extended π-conjugated architectures once conditions are optimized. There is a small red shift apparent in the UV–visible absorption spectra of Zn–P–C_{60} **6** relative to Zn–P **5**, but no conclusive evidence for any ground-state interaction between the two π-systems was found. Recent transient absorption studies, to be published separately, show conclusively that the efficient quenching of the porphyrin fluorescence by the attached fullerene moiety in this molecular wire is due to photoinduced electron transfer (ET), to give a charge separated state $ZnP^{+\cdot}$-alkyne-$C_{60}^{-\cdot}$. The fluorescence lifetime measurements support the notion that the triple bond is a very effective mediator of electronic interaction between porphyrin and fullerene moieties.

EXPERIMENTAL

General methods

All commercially available reagents were used as received unless noted otherwise. Anhydrous toluene (containing < 0.001% water) was purchased from Aldrich and was used as received. Tetrahydrofuran was over potassium metal with benzophenone indicator prior to use. ^{1}H NMR spectra for **1**–**6** were obtained on a Varian 200 MHz NMR instrument with tetramethylsilane (TMS) as an internal standard. Mass spectra for **1**–**6** were obtained using a Bruker Daltronics MALDI-TOF mass spectrometer. Fluorescence measurements on **5** and **6** were obtained using a Hitachi F-2500 spectrofluorimeter and data were acquired on a Hewlett-Packard 8453 UV–visible spectrophotometer. Fluorescence lifetimes were measured by time-correlated single photon counting on (TCSPC) on a PicoQuant FluoTime-100 compact fluorescence lifetime spectrometer.

Synthesis of 1-ethynyl-2-methyl[60]fullerene 2 (Scheme 1)

*1-(Trimethylsilyl)ethynyl-2-methyl[60]fullerene (**1**).* To a deoxygenated solution of C_{60} (200 mg, 0.28 mmol) in anhydrous toluene (220 mL) was added lithium(trimethylsilyl)acetylide (1.8 mL, 0.9 mmol) with vigorous stirring. The mixture was stirred at room temperature for ca 1.5 h under an argon atmosphere. To the mixture was added iodomethane (0.2 mL, 0.32 mmol) and subsequently dry tetrahydrofuran (50 mL). The mixture was heated at 40 °C for 3 h. The reaction mixture was filtered through a silica gel column using toluene as the eluent. The solvent was removed under reduced pressure and the crude product was dissolved in chloroform and filtered through a silica funnel using cyclohexane as the eluent. The solvent was removed under reduced pressure, and the residue was dissolved in chloroform and precipitated with hexanes to afford **1** (52%) as a brown solid. ^{1}H NMR ($CDCl_3$): δ(ppm) 0.44 (s, 9H, Si-CH_3), 3.43 (s, 3H, CH_3). MS (MALDI-TOF): *m/z* 719 [C_{60}], 815 [$M^+ - CH_3$], 831 [M^+] (calcd 832.07).

*1-Ethynyl-2-methyl[60]fullerene (**2**).* To a solution of **1** (80 mg, 0.096 mmol) in tetrahydrofuran (120 mL) and methanol (24 mL) was added K_2CO_3 (50 mg). The reaction vessel was flushed with nitrogen for 10–15 min at room temperature with vigorous stirring and was then heated at reflux for ca 3–4 h. The mixture was cooled and filtered through a silica funnel using CS_2 as eluent. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with cyclohexane as the eluent. Finally, the product was precipitated twice using CS_2–hexanes to afford **2** as a brown solid (50%). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.06 (s, 1H, CC–H), 3.49 (s, 3H, CH_3). MS (MALDI-TOF): *m/z* 719 [C_{60}], 744 [$M^+ - CH_3$], 759 [M^+], (calcd 760.04).

Synthesis of zinc(II) 5-{4-[(trimethylsilyl)ethynylphenyl]-10,15,20-tris(3,5-di-*tert*-butylphenyl)}porphyrin 4 (Scheme 2)

*5-{4-[(Trimethylsilyl)ethynylphenyl]-10,15,20-tris(3,5-di-tert-butylphenyl)}porphyrin (**3**).* To a refluxing solution of 3,5-di-*tert*-butylbenzaldehyde (4.7 g, 21 mmol) and 4-(trimethylsilylethynyl)benzaldehyde (1.8 g, 8.8 mmol) in glacial acetic acid (200 mL) and nitrobenzene (120 mL) was added pyrrole (2 mL) through a dropping funnel. The mixture was heated at reflux for 1 h followed by vacuum distillation to remove the solvents from the reaction vessel. The mixture was cooled, washed with methanol and filtered through a silica funnel with methylene chloride as eluent. The solvents were removed under reduced pressure to give the crude porphyrin **3**, which was not purified prior to metallation.

*Zinc(II) 5-{4-[(trimethylsilyl)ethynylphenyl]-10,15,20-tris-(3,5-di-tert-butylphenyl)}porphyrin (**4**).* To a solution of crude **3** in chloroform (250 mL) and methanol (125 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (5.0 g). The mixture was heated at reflux for 4 h, cooled, filtered, concentrated and chromatographed on silica gel with hexane–CH_2Cl_2 (4:1) to afford a purple solid (yield not determined). ^1H NMR ($CDCl_3$): δ (ppm) 0.40 (s, 9H, Si–CH_3), 1.55 (s, 54H, *t*-Bu–H), 7.81 (s, 3H, *p*-*t*-BuPh–H), 7.89 (d, 2H, *m*-H–PhCCTMS), 8.12 (s, 6H, *o*-*t*-BuPh–H), 8.12 (d, 2H, *o*-H–PhCCTMS), 9.03 (m, 8H, pyrrole–H). MS (MALDI-TOF): *m/z* 1108 [M^+] (calcd 1108.58).

*Zinc(II) 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-tert-butylphenyl)porphyrin (**5**).* To a solution of **4** (60 mg, 54 μM) in tetrahydrofuran (8 mL) was added tetrabutylammonium fluoride (260 mg, 1 mmol) in tetrahydrofuran (1 mL). The mixture was stirred at room temperature for 5–10 min. The mixture was filtered, concentrated and washed twice with methanol to yield a purple crystalline solid (95%). UV–visible ($CHCl_3$): $\lambda_{max} = 424$ nm. ^1H NMR ($CDCl_3$): δ (ppm) 1.54 (s, 54H, *t*-Bu–H), 7.80 (s, 3H, *p*-*t*-BuPh–H), 7.81 (d, 2H, *m*-H–PhCCTMS), 8.10 (s, 6H, *o*-*t*-BuPh–H), 8.11 (d, 2H, *o*-H–PhCCTMS), 8.97 (m, 8H, pyrrole–H). MS (MALDI-TOF): *m/z* 1037 [M^+] (calcd 1036.54).

Synthesis of Zinc(II) 5-(4-ethynylphenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin–1-ethynyl-2-methyl[60]fullerene-dyad 6 (Scheme 3)

To a solution of **2** (15 mg, 19.7 μM) and **5** (10 mg, 9.6 μM) in chlorobenzene (30 mL) at room temperature were added CuCl (208 mg, 2.1 mmol) and TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) (0.3 mL, 2 mmol) under a dry oxygen atmosphere. The reaction mixture was stirred at room temperature for 30 min and filtered through a silica funnel using toluene and CS_2 as eluents (the C_{60} homocoupled product was retained on the silica). The solution was concentrated to 3 mL and the product was purified by repeated preparative thin-layer chromatography on silica using cyclohexane followed by hexane–CH_2Cl_2 (3:1) to afford a non-fluorescent, brown solid, which was pure according to TLC analysis. UV–visible ($CHCl_3$): $\lambda_{max} = 256, 425$ nm. ^1H NMR ($CDCl_3$): δ (ppm) 1.55 (s, 54H, *t*-Bu–H), 7.79 (s, 3H, *p*-*t*-BuPh–H), 8.08 (s, 6H, *o*-*t*-BuPh–H), 8.32 (d, 2H, *m*-H–PhCCTMS), 8.54 (d, 2H, *o*-H–PhCCTMS), 9.03 (d, 4H, pyrrole–H), 9.08 (d, 4H, pyrrole–H). MS (MALDI-TOF): *m/z* 1795 [M^+] (calcd 1794.55).

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