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Synthesis of corrole-fullerene dyads *via* [4+2] cycloaddition reaction

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Three corrole-fullerene dyads were prepared by treating anthracene-functionalized corroles with fullerene. Their structures were characterized by 1D- and 2D-NMR spectra and mass spectra. In the preliminary photo physical study of 3a by state- and transient fluorescence spectroscopy, the excited corrole unit was quenched due to the introduction of fullerene. TD-DFT calculation theoretically indicated that the electron transfer occurs from the excited corrole to fullerene.

Natural tetrapyrrolic macrocycles are some of the most predominant pigments owing to their essential biological roles in life and life cycle, such as chlorophylls, heme, factor 430 and cobalamin.[1] Among them, cobalamin is featured with a framework of corrin which resembles the porphyrin structure with absence of one *meso*-carbon and presence of saturated carbon-edge. The aromatic analogue of corrin is corrole. Thus, corrole is regarded as a structural link between porphyrin and corrin. Corroles were first prepared in the labs of A.W. Johnson as synthetic precursors of corrins.[2, 3] In the past 10 years, with the breakthrough on the efficient synthetic strategies of corrole,[4-8] these new tetrapyrrolic macrocycle-based compounds have been receiving considerable attentions. More and more applications of corrole derivatives have been discovered in catalysis,[9] photochemical sensors,[10] medicine [11] and electron/energy transfer systems.[12-14]

On the other hand, inspired by the role of chlorophylls or bacteriochlorophylls in the natural photosynthesis as the main pigment to harvest light and donate energy/electron,[15] many artificial photosynthetic reaction centers, using porphyrin as energy/electron donor, have been synthesized to mimic certain aspects of photosynthesis, and investigated carefully to understand the different

factors in influencing the energy/electron transfer procedure.[16] However, the requirement for improving the performance and increasing the variety of such donor-acceptor systems has promoted the use of other tetrapyrrolic macrocycles in the artificial photosynthetic reaction center. Keep this in mind, corrole, a tribasic aromatic tetrapyrrolic macrocycle, becomes one of the best electron/energy donor substitutes for porphyrin due to their interesting properties, e.g. low oxidation potentials, high fluorescence quantum yields, intense absorption throughout long wavelength area.[17-20] As a choice of electron/energy acceptor, fullerene has been in control of this field due to the appropriate redox potential and small reorganization energy in electron-transfer reaction.[21, 22] Therefore, the combination of corrole and fullerene used for artificial photosynthetic reaction center is of great value to better understand the photo-induced electron/energy transfer reaction.

The artificial photosynthetic reaction centers using corrole as an energy/electron donor and fullerene as an energy/electron acceptor have emerged recently but still with few reports.[17, 23-28] In relation to our previous work on porphyrins [29, 30] and *tetra*-sulfolenocorrole which was treated with fullerene at high temperature to form the *β*-linked corrole-difullerene triad,[25] we here describe the synthesis of *meso*-linked corrole-fullerene dyad by [4+2] cycloaddition reaction and the preliminary study of the corrole-fullerene dyads by UV-Vis and fluorescence spectroscopy and theoretical calculation (TD-DFT) as potential artificial photosynthetic reaction centers.

After several years efforts, various fullerene modification strategies have been developed.[31] Cycloaddition reactions, e.g. cyclopropanation, and [3+2] and [4+2] cycloaddition reaction,

proved to be one of the most efficient method to functionalize
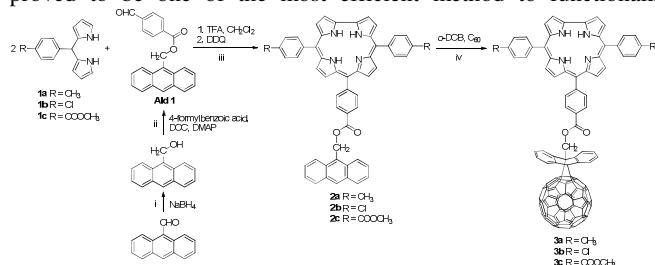
Scheme 1 The synthetic route for the construction of corroles and corrole-fullerene dyads (i: NaBH$_4$, THF, reflux, ~ 2 h, 99 %; ii: 4-formylbenzoic acid, DCC, DMAP, CH$_2$Cl$_2$, 28 h, 82 %; iii: 28 mM TFA in CH$_2$Cl$_2$ 10 h, then DDQ 2 h, 7 - 10 %; iv: o-dichlorobenzene, N$_2$, 5 days, 35 - 46 %.

fullerene at 6,6-ring junctions.[32, 33] In our work, we selected anthracene as the reactive substrate to catch fullerene and furnish covalently linked corrole-fullerene dyad. A flexible OCH$_2$ group was designed as a part of the donor-acceptor linkage to make the compound to have appropriate molecular arrangement in space. **Scheme 1** shows the synthetic route for corrole-fullerene dyads by using aromatic aldehyde (**Ald1**) bearing an anthracene group and the corresponding dipyrromethane (**1**) as key components to construct the anthracene-functionalized corroles *via* '(2+1)-approach'. In detail, condensation of **1a** with **Ald1** in 2 : 1 ratio in the presence of TFA in CH$_2$Cl$_2$ at room temperature, and subsequent in situ oxidation of the obtained intermediate with dicyanodichloro-benzoquinone (DDQ), gave the corrole **2a** as a deep green solid in 8% yield after chromatography purification and crystallization from CH$_2$Cl$_2$ / n-hexane. By the same procedure as that described for the preparation of **2a**, the analogous corroles **2b** and **2c** were obtained in 7 - 10 % yield by using dipyrromethanes **1b** and **1c**, respectively (**Scheme 1**). Finally, a deoxygenated solution of corrole **2a** and fullerene (7.5 mol eq.) in 1,2-dichlorobenzene was slowly stirred under darkness and the corresponding corrole-fullerene dyad **3a** was

then formed. Treatment of **2b** or **2c** with C$_{60}$ was also performed, and **3b** and **3c** were obtained in a yield of 30 - 42%. However, these [4+2] cycloadducts are not stable at room temperature in solution and a reverse reaction of [4+2] cycloaddition was observed in the CDCl$_3$ solution of **3b**, which decomposed to **2b** slowly (10 days). Meanwhile, a reference compound **AnC$_{60}$** has been synthesized in a yield of 60 % (Scheme 2).
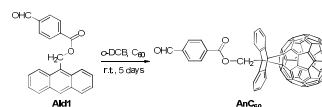
**Scheme 2** The synthetic route of the reference compound **AnC$_{60}$**.

The structures of **2a-c** and **3a** were established by analysis of 1D- and 2D-NMR spectroscopy. **Table 1** summarizes partial chemical shifts of **2a** and **3a** in their ^{1}H-NMR spectra. In the spectrum of **2a**, one singlet at 2.66 ppm (the methyl group) was observed at high field as well as four sets of doublet at low field with the typical coupling constant (J = 4.0 Hz) for periphery pyrrolic hydrogens. The singlets of OCH$_2$ and An10H (see Table 1 for the labeling of carbons in the compound) were found at 8.61 and 6.58 ppm, respectively. A comparison of the chemical shifts and the resonance patterns of OCH$_2$ and An10H in compounds **2a** and **3a** were informative. When compared to the two singlets due to OCH$_2$ and An10H in **2a**, in the spectrum of **3a**, the signal of OCH$_2$ does not move significantly, while the other hydrogen (An10H) in **3a** resonated at a higher chemical shift of 5.89 ppm. Furthermore, the singlet due to OCH$_2$ in **3a** becomes broader. These results suggested the vanishing of the de-shielding effect of the aromatic anthracene unit on An10H in **3a**, which resulted from the loss of the aromaticity of anthracene unit after [4+2] cycloaddition reaction. Also, the broader OCH$_2$ singlet in **3a** indicated the existence of fullerene nearby.[25, 34] The above-mentioned spectrum changes were also observed when we compared the ^{1}H-NMR spectra of **Ald1** and **AnC$_{60}$** (**Fig. S1** and **Fig. S2**).

Table 1 Partial chemical shift values of **2a** and **3a**

|		**2a** ([1]H / [13]C)	**3a** ([1]H / [13]C)	**Ald1** ([1]H / [13]C)	**AnC$_{60}$** ([1]H / [13]C)
	An1&An8	8.61 / 124.4	7.95 / 124.9	8.43 / 123.5	7.75 / 124.0
	An2&An7	7.68 / 127.1	7.56 / 127.6	7.61 / 126.8	7.49 / 127.2
	An3&An6	7.56 / 125.4	7.56 / 127.6	7.52 / 125.0	7.54 / 127.2
	An4&An5	8.10 / 129.4	7.85 / 126.0	8.07 / 129.0	7.83 / 125.8
	An10	8.61 / 129.5	5.89 / 58.8	8.56 / 129.4	5.89 / 58.5
	An11&An14	- / 131.6	- / 139.6	- / 130.9	- / 139.4
	An12&An13	- / 131.7	- / 141.3	- / 131.1	- / 140.7
	unsaturated C of fullerene	- / -	- / 74.6	- / -	- / 74.2
	OCH$_2$	6.58 (sharp s.) / 59.8	6.45 (broad s.) / 65.2	6.44 (sharp s.) / 59.5	6.35 (broad s.) / 65.3

Furthermore, HSQC spectrum of **3a** shows the correlation between the singlet of An10H at 5.89 ppm and the carbon signal at 58.8 ppm (An10C), while in the HMBC spectrum of **3a**, the singlet of An4H at 7.85 ppm correlated to the carbon which resonates at 58.8 ppm (An10C), the singlet of An10H at 5.89 ppm correlated to the carbon with a resonance at 74.6 ppm, i.e. the typical chemical shift value of an aliphatic quatemary carbon in a [4+2] cycloaddition reaction modified fullerene.[35] In addition, similar ^{1}H and ^{13}C-chemical shift values were obtained for An1-10 in both corrole-fullerene dyad **3a** and the model compound **AnC$_{60}$** (see **Table 1**). These observations in homo- and heteronuclear correlations in **3a** and **AnC$_{60}$**, including the methine carbon signal (An10C) and one quatemary carbon in fullerene as described above, strongly supported the assigned

compound structure anddemonstrated the formation of the corrole-fullerene dyad (see **Fig. 1**).
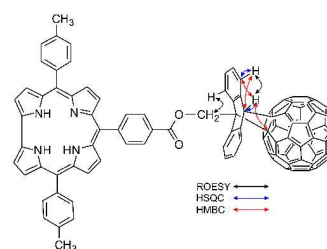

Fig. 1 Key H-H and H-C couplings of **3a** obtained from 2D NMR.

The corrole-fullerene compound **3a** was further characterized by mass spectrum, which confirmed its molecular formula as $C_{115}H_{40}N_4O_2$ by a weak pseudo-molecular ion at $m/z = 1509.3$ $[M+H]^+$ (**Fig. 2**). Meanwhile, certain fragments were also picked up to identify the cleavage sites. For instants, the fragments at $m/z = 720.0$, 788.3 should be generated from the splitting of the newly formed bonds in the [4+2] reaction (**Fig. 2** Type A). This indicated the occurrence of retro-[4+2] cleavage. Also, the fragments at $m/z = 553.1$, 978.4 (+ Na^+) should be resulted from the cleavage of the bond between the carbonyl and benzo groups extended at the corrole 10-position (**Fig. 2** Type C). Besides, one fragment obtained from the breaking of the alkoxy bond (**Fig. 2** Type B) is found at $m/z = 598.1$. Meanwhile, the mass spectrum of **3b** also shows similar type of cleavage (see **Fig. S10**).
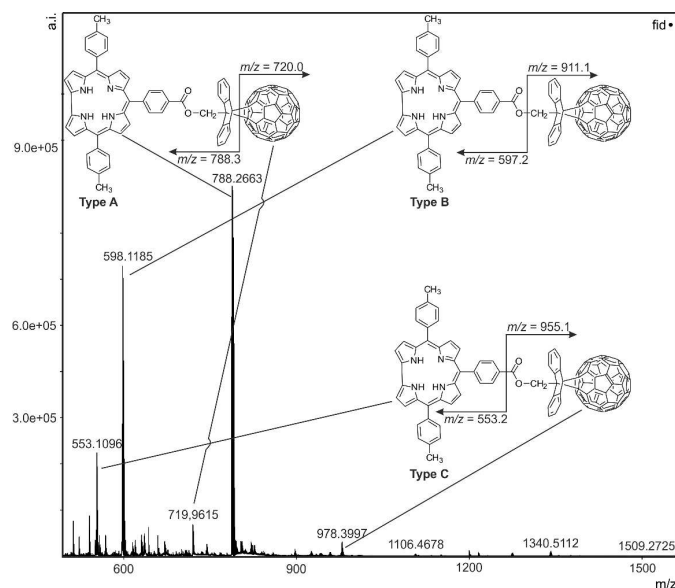

Fig. 2 The MALDI-TOF mass spectrum of corrole-fullerene dyad **3a** (without matrix).

Next, the preliminary study on the photo physical properties of the corrole-fullerene dyad **3a** was performed. The UV/Vis-spectra of **3a**, its components **2a**, **Ald1** and reference compound **AnC$_{60}$** in CH_2Cl_2 are shown in **Fig. 3**. By comparing the spectra of **Ald1** and **2a**, it is found that the spectrum of **2a** is essentially a combination of the absorptions of a normal corrole and an anthracene. The new sharp absorption at 257 nm and the "saw-teeth" absorption (330 nm - 400 nm) in the spectrum of **2a** should be attributed to the absorption of anthracene group. When compared to the absorption spectrum of a typical corrole, **2a** also shows a strong Soret band at 420 nm and three Q bands absorption in the range 500 to 700 nm. Further, the spectrum of **3a** displays a slight difference than that of **2a** with the disappearance of the anthracene's absorption (257 nm and "saw-teeth" part) and appearance of a broad absorption of fullerene (258.5 nm, 314.0 nm and a very weak one near 705 nm). However, the corrole-fullerene dyad **3a** did not show some new absorption and its spectrum is the superposition of absorption of novel corrole and the reference component **AnC$_{60}$**. This indicated no intramolecular electronic interaction between corrole and fullerene units in the ground state of **3a**.
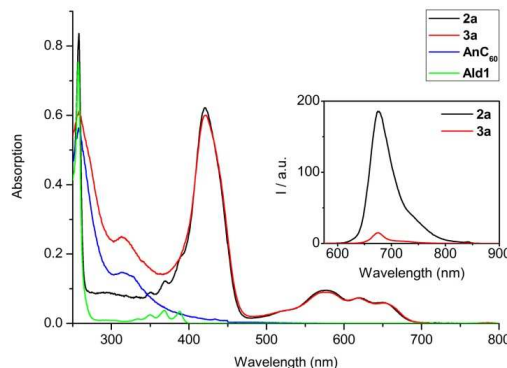
Fig. 3 UV-Vis spectra of **Ald1**, **AnC$_{60}$**, **2a** and **3a** in CH_2Cl_2, and fluorescence emission spectra (inset) of **2a** and **3a** in CH_2Cl_2 (excited at 422 nm).

In the emission spectrum of **2a** (**Fig. 3**, inset), the characteristic fluorescence of the corrole core is observed, which has been effectively quenched in that of **3a**. Meanwhile, **Fig. 4** shows the fluorescence decay curves of **2a** and **3a** in term of the corrole fluorescence scope. The time decay of corrole emission decreases significantly after introduction of fullerene, where the fluorescence lifetimes of **2a** and **3a** are found to be 2.57 ns and 0.75 ns, respectively. The decreasing of the fluorescence intensity and fluorescence lifetime of the corrole unit in **3a** (about 3 times) with respect to those of the precursor **2a** should be taken as a sign of efficient quenching of the photo-excited corrole by the closely attached fullerene moiety in **3a**. Hence, a proposed photo-induced electron transfer should occur between corrole and fullerene as described in other corrole-fullerene conjugates. [17]
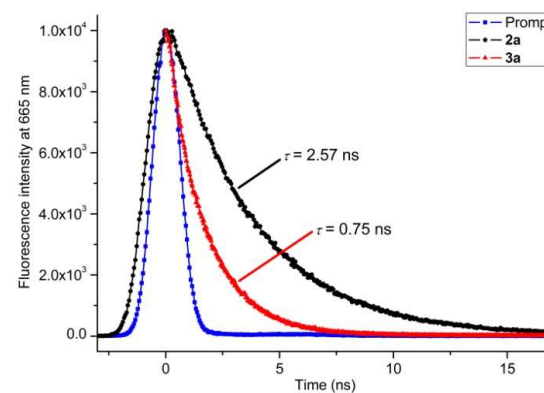

Fig. 4 Fluorescence decay curves of **2a** and **3a** in CH_2Cl_2 (excitation at 366 nm, detection at 667 nm).

In order to further understand the electronic and geometrical structures of the corrole-fullerene dyad, *ab initio* quantum mechanical calculations were performed with TD-DFT variant hybrid density functional theory (B3LYP) in conjunction with the 6-31G (d) basis set as implemented in the Gaussian 09 program package.[36] The distances of "center to center" and "edge to edge", calculated from the geometrical structure of **3a**, are 15.8 Å and 10.2 Å, respectively (see the energy-optimized structure of **3a** shown in **Fig. S11**). In addition, **Fig. 5** shows the frontier highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) generated from theoretical calculation. The result is similar to those reported previously.[17, 27] The HOMO (-4.75 eV) locates on the corrole moiety, while the LUMO (-3.07 eV) resides totally on the

fullerene cage of **3a**. Furthermore, part of the HOMO is also observed on the *meso*-phenylene spacer of the dyad, suggesting considerable interaction between the donor and acceptor units. Thus, the calculated distribution of MO manifested the proposed intramolecular electron transfer from the excited corrole to the fullerene in gaining of charge-separated state corrole$^{\cdot +}$-$C_{60}^{\cdot -}$.
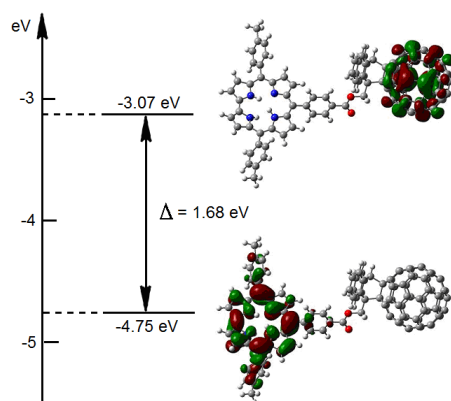
Fig. 5 The HOMO, LUMO, HOMO-LUMO gap and energy level of corrole-fullerene dyad **3a**.

Conclusions

In conclusion, we reported the synthesis and characterization of novel corrole-fullerene dyad **3a-c**. By tracing the fragments in mass spectrum, the possible decomposition route was deduced. Next, the preliminary photo physical properties of the corrole-fullerene dyad have been studied. Strong fluorescence quenching and fluorescence lifetime reducing of corrole core in **3a** indicated that electron transfer could take place between excited corrole and fullerene. TD-DFT calculation was also employed to analyze the electronic and geometry structures. The desired distribution of MO theoretically confirmed that the dyad **3a** has a strong propensity for intramolecular electron transfer from corrole to fullerene cage.

Notes and references

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