

Molecular Tweezer Based on Perylene and Crown Ether for Selective Recognition of Fullerenes

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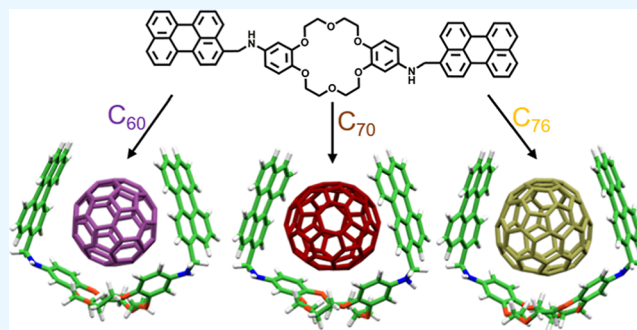
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ABSTRACT: A molecular tweezer *trans*-di(perylene-3-ylmethanaminobenzo)-18-crown-6 (DP-18C6) incorporating two perylene subunits in a single crown ether core was designed and synthesized as a host for fullerenes. Through the cooperative effect of the perylene subunits and the crown ether moiety, DP-18C6 can efficiently recognize fullerenes including C₆₀, C₇₀, and C₇₆. ¹H NMR titration and fluorescence titration experiments demonstrated that DP-18C6 can effectively grasp the fullerene molecule to form a 1:1 host–guest complex. Density functional theory calculations revealed the presence of intermolecular π – π interactions between the perylene subunits of DP-18C6 and the fullerene molecule. More importantly, DP-18C6 exhibited remarkably high binding selectivity for higher fullerenes over C₆₀, revealing potential application for the separation of fullerenes by means of host–guest interactions.



revealing potential application for the separation of fullerenes

1. INTRODUCTION

The research on fullerene receptors based on noncovalent interactions has become an active area since the emergence of supramolecular chemistry.^{1–4} To date, a number of supramolecular assembled receptors have been developed as fullerene hosts including macrocycles,^{5,6} bowl-shaped molecules,⁷ and molecular cages.^{8,9} Fullerene hosts are usually composed of planar or concave aromatic units that comprise porphyrins,¹⁰ calixarene,¹¹ corannulenes,¹² tetrathiafulvalene,¹³ and so on, which are known for their favorable π – π interactions with fullerenes. Because of the similarity among different sized fullerenes, the host–guest complexes formed by hosts and fullerenes generally exhibit similar properties, which make it difficult for fullerene hosts to selectively recognize different sized fullerenes.

As the first generation of macrocyclic hosts, crown ethers have attracted extensive attention for their ability to bind inorganic or organic guests to form various supramolecular architectures.^{14–17} Mukherjee et al.¹⁸ disclosed that the binding strength of crown ethers with fullerenes depended on the cavity sizes of the crown ethers. Since then, a series of crown ether derivatives as fullerene hosts have been explored, including porphyrins,¹⁹ tetrathiafulvalene,²⁰ and pentiptycene.²¹ Perylene is well-known for its outstanding chemical, thermal, and photophysical stability.^{22,23} The large π -conjugated structure of perylene and its derivatives makes them favorable candidates for fullerene hosts.^{24–26} Although crown ether derivatives or perylene derivatives can serve as

excellent fullerene hosts, there are few reports that crown ether or perylene derivatives as fullerene hosts can selectively recognize different sized fullerenes.

Herein, a novel molecular tweezer *trans*-di(perylene-3-ylmethanaminobenzo)-18-crown-6 (DP-18C6) incorporating two perylene subunits in a single crown ether core has been rationally designed and synthesized for selective recognition of different sized fullerenes. The crown ether moiety can not only act as a central scaffold to construct molecular architectures but can also bind with fullerene molecules. The two perylene subunits can act as pincers to efficiently catch the fullerene ball through π – π interactions. Thanks to the synergistic effect between the crown ether core and the perylene subunits, the molecular tweezer DP-18C6 can efficiently bind different sized fullerenes including C₆₀, C₇₀, and C₇₆. Especially, DP-18C6 exhibited better recognition of higher fullerenes with Stern–Volmer constant 1 order of magnitude higher for C₇₀ and C₇₆ versus C₆₀, which has potential application in the separation of fullerenes by means of host–guest interactions.

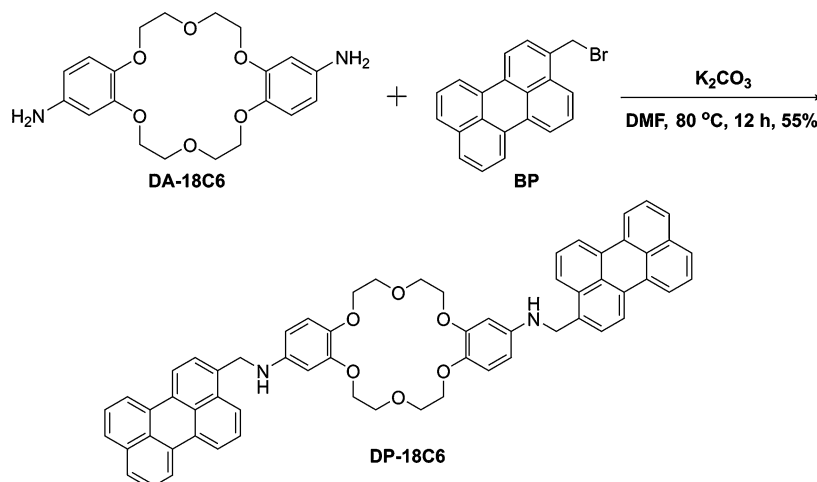
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Scheme 1. Synthesis of DP-18C6



2. RESULTS AND DISCUSSION

The synthesis of DP-18C6 is shown in Scheme 1. The crown ether core *trans*-di(aminobenz)-18-crown-6 (DA-18C6) was prepared by previously reported procedures.²⁷ The perylene subunit 3-(bromomethyl)perylene (BP) was synthesized through the reaction of perylene-3-ylmethanol with PBr_3 in tetrahydrofuran to give BP in a 58% yield (Scheme S1), which was characterized by 1H and ^{13}C NMR spectroscopy (Figures S1 and S2). Then, the alkylation reaction of DA-18C6 with BP in *N,N*-dimethylformamide in the presence of K_2CO_3 under an argon atmosphere at 80 °C afforded the target DP-18C6 in a 55% yield. Full details relating to the syntheses of BP and DP-18C6 are provided in the Supporting Information. DP-18C6 was fully characterized by 1H and ^{13}C NMR spectroscopy with full assignment of spectra provided from two-dimensional NMR experiments including correlation spectroscopy and heteronuclear single quantum coherence, which was further confirmed by high-resolution mass spectrometry (Figures S3–S7).

The formation of the host–guest complexes between DP-18C6 and fullerenes was first demonstrated by 1H NMR titration of DP-18C6 with fullerenes (C_{60} , C_{70} , and C_{76}). As shown in Figures 1 and S8–S10, the addition of fullerenes

(C_{60} , C_{70} , and C_{76}) induced upfield shifts of the perylene protons signals, which indicate the existence of π – π interactions between perylene subunits and fullerenes.^{28,29} In particular, the protons of the secondary amine showed very significant upfield shifts, owing to the formation of the host–guest complexes.^{29,30} Moreover, the signals of the ethylene protons of the crown ether moiety were slightly shifted downfield upon the addition of fullerene (C_{60} , C_{70} , and C_{76}), indicating weak n – π interactions between the crown ether moiety and fullerenes.³¹ Further evidence for the formation of host–guest complexes was provided by correlation spectroscopy spectra of DP-18C6 and equimolar mixtures of DP-18C6 and fullerene (C_{60} , C_{70} , and C_{76}). As shown in Figure S11a, DP-18C6 showed notable cross-peak signals due to the spin–spin coupling between methylene and secondary amine. However, when equimolar fullerene (C_{60} , C_{70} , and C_{76}) was added to DP-18C6, the corresponding cross-peak signals disappeared (Figures S11 and S12), indicating that the formation of the host–guest complex interfered with the spin–spin coupling between methylene and secondary amine.

To quantitatively investigate the binding interactions between DP-18C6 with fullerenes (C_{60} , C_{70} , and C_{76}), fluorescence titration experiments were performed. Initially, the UV–vis absorption and fluorescence emission spectra of DP-18C6 in chlorobenzene (PhCl) were investigated (Figures S13 and S14). As displayed in Figure S14, DP-18C6 showed typical perylene emission features with an emission peak at 465 nm and a shoulder peak at 486 nm. However, upon the addition of C_{60} (Figure 2a), the fluorescence intensity of DP-18C6 was slightly decreased because of the fluorescence quenching effect of C_{60} . This result indicates that the interaction of C_{60} with the perylene subunit is weak, which is probably attributed to the negligible electron communication between the electron-poor perylene subunit and the electron-deficient C_{60} .²⁴ By contrast, the fluorescence intensity of DP-18C6 was significantly decreased upon the introduction of C_{70} and C_{76} (Figure 2b,c). Then, to determine the binding stoichiometry of the binding complexes between DP-18C6 and fullerene (C_{60} , C_{70} , and C_{76}), both Stern–Volmer and Job's plot methods were employed. As shown in Figure S15, the Stern–Volmer plot analysis verified the formation of 1:1 complexes between DP-18C6 and fullerene (C_{60} , C_{70} , and C_{76}). The results were consistent with those of Job's plot analysis (Figure S16), in which the maximum points observed

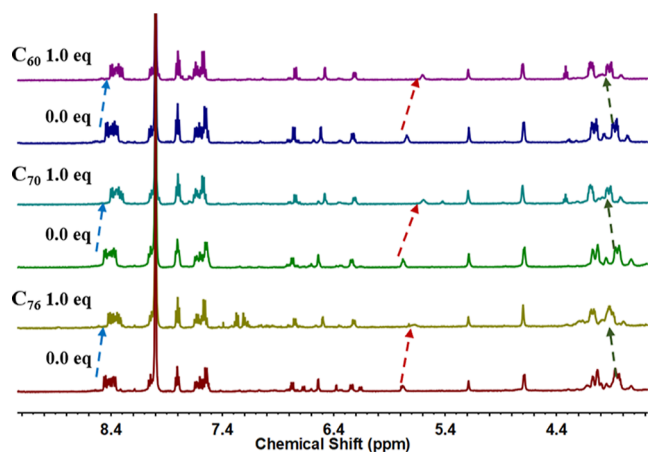


Figure 1. 1H NMR spectra (500 MHz, *N,N*-dimethylformamide- d_7) of DP-18C6 with 1.0 equiv fullerene (C_{60} , C_{70} , and C_{76}) and free DP-18C6.

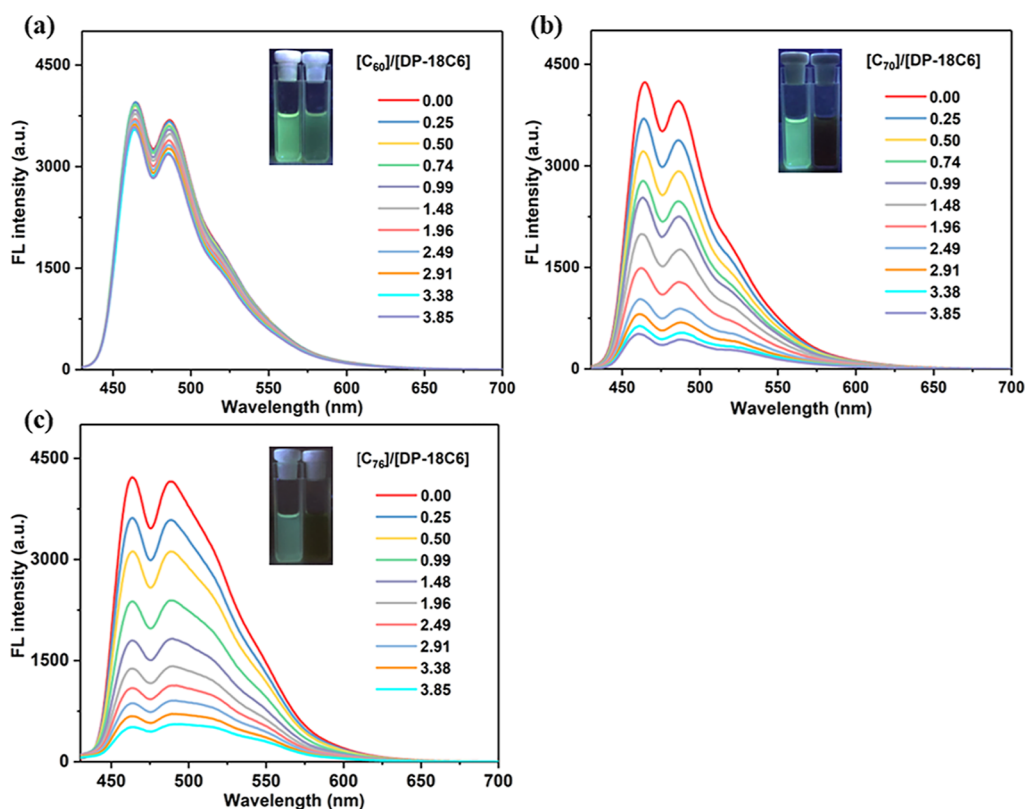


Figure 2. Fluorescence emission spectra ($\lambda_{\text{ex}} = 415 \text{ nm}$) of DP-18C6 ($20 \mu\text{M}$) with the addition of C_{60} (a), C_{70} (b), and C_{76} (c) at different mixing ratios (0–3.85 equiv) in PhCl. Insets: Photographs of the fluorescence of DP-18C6 before (left) and after (right) the addition of fullerene under a UV lamp at 365 nm.

at 0.5, suggesting the 1:1 stoichiometry. According to these titration studies, the Stern–Volmer constants³² for the complexes DP-18C6- C_{60} , DP-18C6- C_{70} , and DP-18C6- C_{76} were determined to be 1.65×10^3 , 3.58×10^4 , and $3.94 \times 10^4 \text{ M}^{-1}$, respectively, indicating that DP-18C6 exhibited selective complexation toward higher fullerenes over C_{60} . Considering that these three fullerenes C_{60} , C_{70} , and C_{76} have different sizes, the selective complexation of DP-18C6 toward higher fullerenes reveals that there is a size effect for DP-18C6 binding with fullerene molecules. The size-dependent effect could be attributed to the better adaptability and stronger π – π interactions between DP-18C6 and higher fullerenes.

In order to investigate the energy process between DP-18C6 and fullerenes (C_{60} , C_{70} , and C_{76}) in the host–guest complexes, deactivation pathways after photoexcitation were examined by femtosecond transient absorption (TA) spectroscopy. The TA spectra of the host–guest complexes in PhCl after a 400 nm laser excitation are shown in Figure 3. In the near-infrared region, with time decay, there are no fingerprint absorption maxima in the 1020–1050, and 1330–1380 nm regions, which is the characteristic absorption peak of one-electron reduced form of C_{60} , and C_{70} , respectively.^{33,34} This proved that there is no electron transfer between DP-18C6 and fullerenes (C_{60} , C_{70} , and C_{76}) in host–guest complexes. With time decay, DP-18C6- C_{60} exhibited an absorption maximum in the 900–1000 nm range, which is the TA characteristic of C_{60} (Figure S17a). Obviously, DP-18C6- C_{70} showed an absorption peak at 960 nm corresponding to the characteristic TA of C_{70} (Figure S17b). Similarly, DP-18C6- C_{76} showed a broad absorption peak extending from 900 to 1000 nm, which is attributed to the TA characteristic of C_{76} (Figure S17c). Then,

by comparing the TA spectra of DP-18C6-fullerene, DP-18C6 (Figure 3d) and fullerenes (C_{60} , C_{70} , and C_{76}) with the 400 nm laser excitation, it showed that the TA spectra of DP-18C6-fullerene were not simple superposition of the TA spectra of DP-18C6 and corresponding fullerenes (C_{60} , C_{70} , and C_{76}). Thus, these results revealed that there is an energy-transfer process between DP-18C6 and fullerenes (C_{60} , C_{70} , and C_{76}) in the host–guest complexes.

To shed light on the interactions between DP-18C6 and fullerenes (C_{60} , C_{70} , and C_{76}), density functional theory calculations were performed. The energy-minimized structures were calculated for DP-18C6- C_{60} , DP-18C6- C_{70} , and DP-18C6- C_{76} . As shown in Figure 4, the DP-18C6 molecule can grasp the fullerene molecule like a tweezer and the two perylene subunits are the clamps of the tweezer. Due to the high symmetry of C_{60} , there is no significant orientational preference in the host–guest complex of DP-18C6- C_{60} . In contrast, C_{70} and C_{76} tend to maximize the contact by exposing their equatorial regions to the DP-18C6 molecule, resulting in stronger π – π interactions between the perylene subunits and the fullerene molecule. This can explain the size effect for DP-18C6 binding with different sized fullerene molecules. As shown in Table S1, the distance between the perylene subunit and the center point of the fullerene cage is basically less than 6.6 Å. This means the distance between perylene subunit and the fullerene surface is less than 3.1 Å (the diameter of C_{60} is 7 Å), which is close enough for strong π – π interactions. The total interaction energy of DP-18C6-fullerene ranges from -53.89 to $-63.23 \text{ kcal mol}^{-1}$. Notably, the total interaction energy of DP-18C6-fullerene increases with the size of

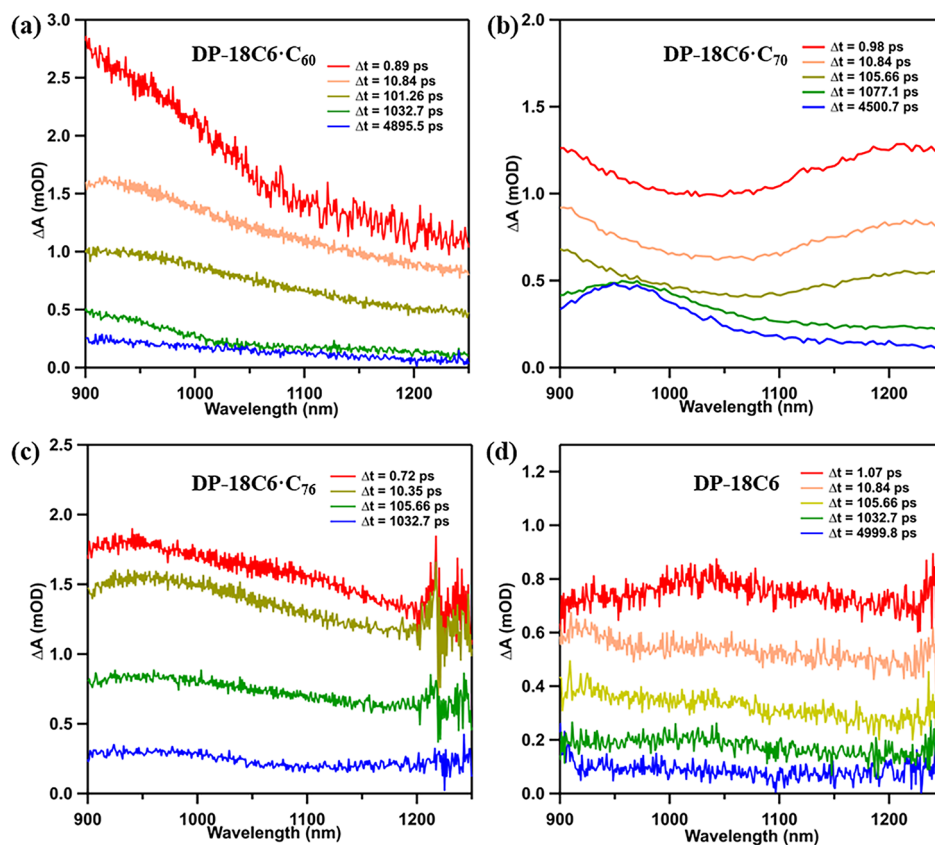


Figure 3. Differential absorption changes (near-infrared region) obtained upon femtosecond pump probe experiments (400 nm) of DP-18C6- C_{60} (a), DP-18C6- C_{70} (b), DP-18C6- C_{76} (c), and DP-18C6 (d) in argon-saturated PhCl with several time delays at room temperature.

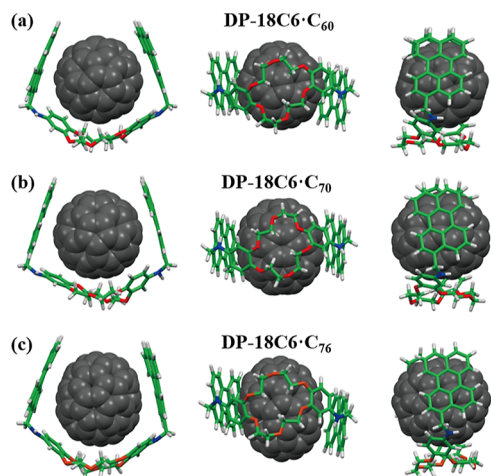


Figure 4. Optimized structures of DP-18C6- C_{60} (a), DP-18C6- C_{70} (b), and DP-18C6- C_{76} (c) at the B3LYP-D3/6-31G(d,p) level. In each column, the panel shows front view, bottom view, and side view, respectively.

fullerenes, that is, the larger is the fullerene size, the higher is the total interaction energy.

To gain further insights into the intermolecular interactions in the host-guest complexes, we calculated the interaction energy between each subunit of DP-18C6 and fullerenes (C_{60} , C_{70} , and C_{76}). According to the fragmentation methods,³⁵ DP-18C6 can be divided into the perylene unit (P) and the crown ether unit (C) by capping the dangling bonds with hydrogen atoms. As a result, the total interaction energy of DP-18C6-

fullerene, namely, $\Delta E_{DP/F}^{int}$, can be divided into three parts, including the interaction energy between the perylene unit and fullerene ($\Delta E_{P/F}^{int}$), the interaction energy between the crown ether unit and fullerene ($\Delta E_{C/F}^{int}$) and the two-body interaction correlation energy between the perylene unit and the crown ether unit (ΔE^{corr}) ($\Delta E_{DP/F}^{int} = \Delta E_{P/F}^{int} + \Delta E_{C/F}^{int} + \Delta E^{corr}$). As shown in Figure 5, the partial interaction energies of the perylene unit and fullerenes (C_{60} , C_{70} , and C_{76}) are generally larger than those of the crown ether unit and

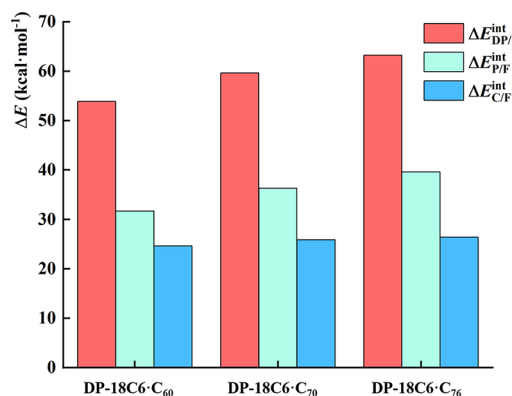


Figure 5. Calculation results of $\Delta E_{DP/F}^{int}$, $\Delta E_{P/F}^{int}$, and $\Delta E_{C/F}^{int}$ in DP-18C6-fullerene interaction systems. All values in the figure are absolute values. $\Delta E_{DP/F}^{int}$ (red columns), $\Delta E_{P/F}^{int}$ (green columns), and $\Delta E_{C/F}^{int}$ (blue columns) represent the interaction energies between DP-18C6 and fullerene, the perylene unit and fullerene, the crown ether unit and fullerene, respectively.

fullerenes, revealing that the perylene unit makes a larger contribution to the total interaction energy than the crown ether unit ($\Delta E_{P/F}^{\text{int}} > \Delta E_{C/F}^{\text{int}}$). In addition, $\Delta E_{DP/F}^{\text{int}}$ increases with $\Delta E_{P/F}^{\text{int}}$, whereas $\Delta E_{C/F}^{\text{int}}$ changes slightly. These results indicated that the variation in the total interaction energies mainly depends on the changes in the partial interaction energies of the perylene unit and fullerenes.

3. CONCLUSIONS

In summary, we have reported a novel molecular tweezer DP-18C6 bearing two perylene units in a crown ether core that shows high affinity toward different sized fullerenes including C₆₀, C₇₀, and C₇₆. ¹H NMR titration and fluorescence titration experiments demonstrated that DP-18C6 can effectively grasp the fullerene molecule to form a 1:1 host–guest complex. More importantly, DP-18C6 exhibited strong complexation toward higher fullerenes (C₇₀, and C₇₆) over C₆₀. The femtosecond TA experiments revealed that there is an energy-transfer process between DP-18C6 and fullerenes in the host–guest complexes. Theoretical calculations indicated that the contribution of the perylene unit in DP-18C6 is larger than that of the crown ether unit in the intermolecular interactions between DP-18C6 and fullerenes. This work implies that DP-18C6 can selectively recognize different sized fullerenes and have potential application in the separation of fullerenes by means of host–guest interactions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c03860>.

Synthesis and characterization of DP-18C6, titration experiments, TA spectra, and density functional theory computational results (PDF)

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Notes

The authors declare no competing financial interest.

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