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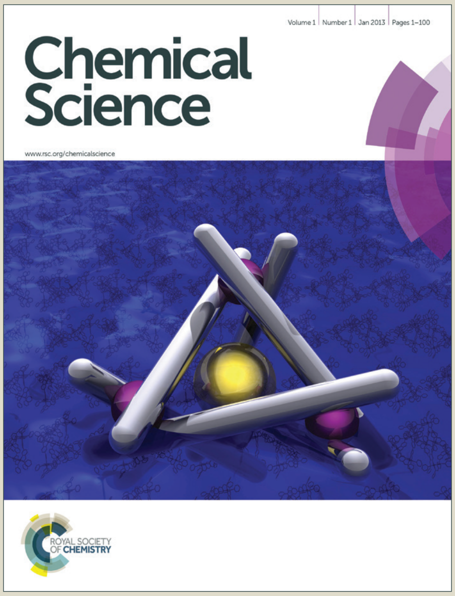

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Supramolecular Free Radicals: Near-infrared Organic Materials with Enhanced Photothermal Conversion

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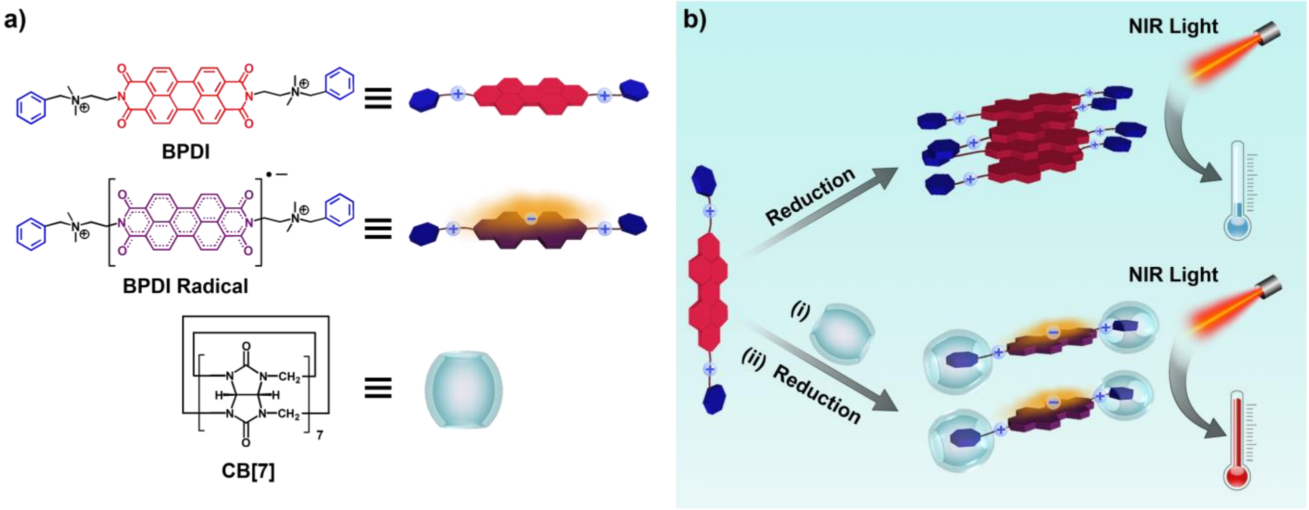
A novel kind of supramolecular free radical with significantly improved free radical yield and enhanced near-infrared (NIR) photothermal conversion is fabricated. Perylene diimide (PDI) can undergo chemical reduction to generate PDI radical anions. Cucurbit[7]uril (CB[7]), a bulky hydrophilic head, was utilized to encapsulate the two end groups of PDI derivative via the host-guest interactions, thus hindering its aggregation and suppressing the dimerization and quenching of PDI radical anions in aqueous solution. Due to the increased concentration of radical anions and their absorption above 800 nm, the efficiency of NIR photothermal conversion was significantly improved. Compared with free radicals fabricated by covalent chemistry, the supramolecular free radical established here can provide a facile approach for the promoted formation of aromatic free radicals, thus opening up a new strategy for the design of NIR photothermal materials with enhanced photothermal conversion.

Introduction

Photothermal materials have various applications, especially for photothermal therapy[1] and light-triggered drug release.[2] For most applications of photothermal materials, they usually have a strong absorption in the near-infrared (NIR) region, as the region from 780 nm to 1300 nm, named "Biological Window", is where most biological tissues are highly transparent.[3] Thus, NIR light is a preferred source to penetrate biological tissues and realize the photothermal conversion *in vivo*. One of the promising candidates for photothermal materials are organic dyes, which absorb NIR light and convert the photo-energy into heat via non-radiative relaxation pathways such as molecular vibrations.[4] Organic dyes not only exhibit considerable heat generation capabilities, but also have several advantages like readily accessibility, stability and potential flexibility for structure design and tunable applications. In the search for more organic systems with NIR absorption, we noticed that delocalized radical anions could be generated from electron-deficient aromatic diimides under chemical or electrochemical reduction, inducing a red shift of the absorption.[5] Among them, perylene diimide (PDI) radical anions have a typical red shift towards the NIR region.[5c, 5d] The inherent reactivity of radical anions and the aggregation of PDI[6] usually cause PDI radical anions to dimerize and quench in aqueous environments, leading to a loss of free radical yield.[7] Many efforts have been devoted to suppress the quenching effect by covalently introducing bulky moieties onto the PDI cores,[8] so that the improvement of PDI radical anion yield is achieved in non-aqueous solvents. To the best of our knowledge, a promoted formation of PDI radical anions by supramolecular strategy in aqueous solution has not yet been reported.

Cucurbit[*n*]urils (CB[*n*]), a family of barrel-shaped macrocyclic hosts, have attracted wide attention on the supramolecular chemistry[9] and other related areas[10] because of their exceptionally firm bindings with cationic species. Due to the large molecular sizes and the hydrophilic exteriors, CB[*n*] have been utilized as non-covalent steric hindrance blocks to optimize the molecular properties.[11] In this study, we have attempted to employ CB[7] to weaken the close stacking of PDI aromatic cores, suppressing the dimerization and quenching of PDI radical anions, and thus improving the free radical yield in aqueous solution. As shown in Scheme 1, a bola-form amphiphile (BPDI) containing PDI as the rigid core was designed and synthesized. The other building block, CB[7], with a suitable cavity for the benzyl moiety, was expected to encapsulate the two end groups of BPDI by the host-guest interactions and then a "dumbbell-shape" supramolecular complex was constructed. As expected, a novel kind of supramolecular free radical was generated via the reduction of the supramolecular complex, and the production of PDI radical anions could be markedly enhanced by the steric hindrance of CB[7]. In addition, the introduction of two quaternary ammonium groups in the BPDI molecule and the encapsulation of CB[7] make the system water-soluble. It is conceivable that the supramolecular free radicals, which could be fabricated in a simple and facile process, have enough solubility and stability in water for the following photothermal conversion. Finally, the NIR photothermal conversion efficiency could be notably promoted by the increased concentration of PDI radical anions with their absorption above 800 nm.



Scheme 1. a) Chemical structures of BPDI, BPDI radical anion and CB[7]. b) BPDI radical anions generated by chemical reduction, leading to low NIR photothermal conversion efficiency (top). The fabrication of the BPDI/(CB[7])$_2$ supramolecular complex by host-guest interactions between CB[7] and two benzyl end groups of BPDI, and the chemical reduction of this supramolecular complex, leading to the promoted formation of supramolecular free radicals with improved NIR photothermal conversion efficiency (bottom).

Results and discussion

Various methods including NMR, fluorescence spectroscopy, UV-Vis spectroscopy and isothermal titration calorimetry (ITC) were employed to confirm the complexation between BPDI and CB[7] in aqueous solutions. As shown in ^{1}H NMR spectra, upon addition of 2 equivalents of CB[7] into BPDI solution, the benzyl proton peaks of BPDI (around 7.5 ppm) shifted upfield as a consequence of CB[7] inclusion. Concurrently, the PDI proton peaks (around 7.9 ppm) shifted downfield because of the weakening of π–π stacking (Figure 1a). This indicates the formation of a host-guest supramolecular complex by the encapsulation of two benzyl end groups of BPDI with CB[7]. Moreover, as indicated in Figure S1, the π–π stacking between the adjacent PDI chromophores caused a significant quenching of fluorescence,[11c] while after the addition of CB[7], the recovery of fluorescence could be observed, suggesting the deaggregating effect of such supramolecular complex.

The UV-Vis spectroscopic titration experiments were performed to quantitatively study the complexation. The concentration of BPDI was fixed at 0.3 mM, and with the addition of CB[7], the π–π stacking between the adjacent PDI chromophores weakened, causing a gradual increase in the characteristic absorption at 540 nm (Figure 1b inset). As shown in Figure 1b, by analysing the absorbance change at 540 nm at different molar ratios, we found that the absorbance nearly stopped increasing after the molar ratio reached 2. So the binding stoichiometry between BPDI and CB[7] is determined to be 1:2.

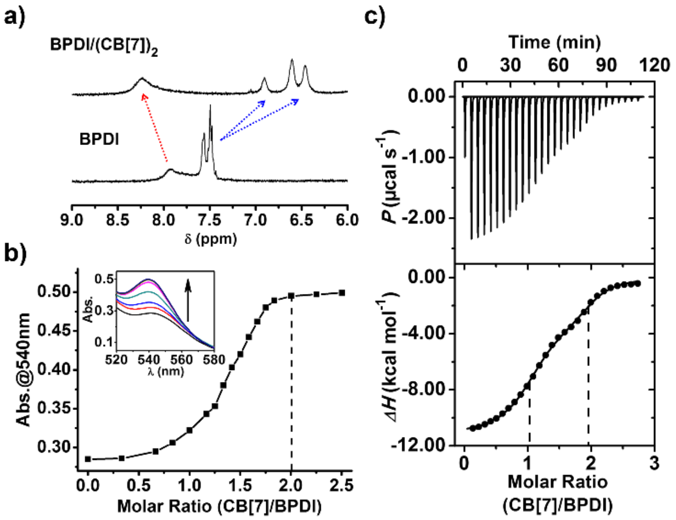


Figure 1. a) Partial ^{1}H NMR spectra of BPDI (0.5 mM) and BPDI/(CB[7])$_2$ (0.5 mM) aqueous solutions. b) UV-Vis titration results of absorbance at 540 nm against the molar ratio of CB[7]:BPDI. Inset: Typical UV-Vis spectral changes of BPDI with the addition of CB[7] in aqueous solution. c) ITC data for the titration of CB[7] into BPDI. c(BPDI) = 0.05 mM, c(CB[7]) = 0.65 mM.

We also used ITC to collect more thermodynamic information about the complexation. From the obtained titration data in Figure 1c, two binding sites could be observed, and the second site corresponded to a molar ratio of 1:2. This indicates that one BPDI molecule with two benzyl end groups can be associated with two CB[7] molecules, which is consistent with the result of the UV-Vis spectroscopic titration. By fitting the data, the binding constant of BPDI with CB[7] is calculated to be 2.9 × 10^{12} M^{-2}. Such strong interactions result from a combination of host-guest interaction and electrostatic attraction between the quaternary ammonium groups in BPDI and the seven carbonyl groups at the edge of CB[7]. Therefore, the host-guest interactions are strong enough for the construction of the BPDI/$(CB[7])_2$ supramolecular complex with well-defined composition.

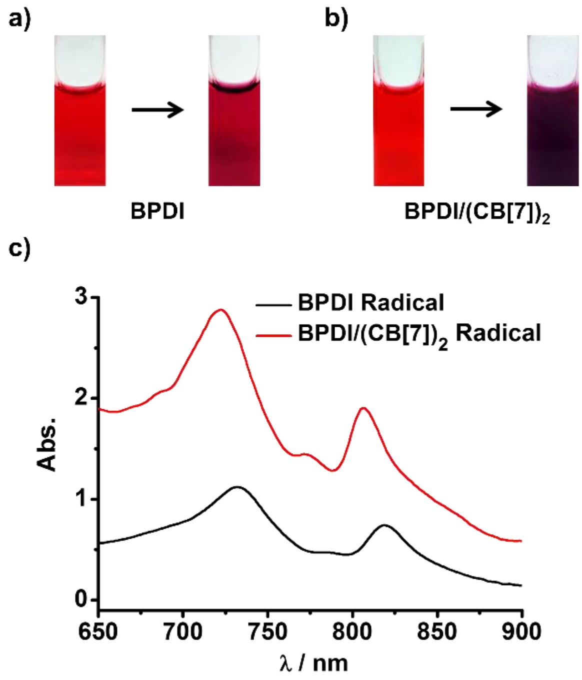


Figure 2. Photographs of the process of radical anion generation from a) BPDI (0.3 mM) or b) BPDI/$(CB[7])_2$ (0.3 mM). c) UV-Vis spectra of the solutions containing BPDI radical anions and BPDI/$(CB[7])_2$ radical anions, respectively.

We wondered if the BPDI/$(CB[7])_2$ supramolecular complex could generate more PDI radical anions than BPDI itself under the same conditions. To answer this question, sodium dithionite ($Na_2S_2O_4$) was selected to reduce BPDI and BPDI/$(CB[7])_2$ in aqueous solutions and produce PDI radical anions, respectively. In a typical process, $Na_2S_2O_4$ solution (in pH 8 borate buffer) was freshly prepared and then injected into a sealed cuvette containing BPDI aqueous solution after a constant bubbling of nitrogen gas for 30 min.[7a] After injection of $Na_2S_2O_4$ with stirring, the color of the BPDI solution changed from red to purplish-red immediately (Figure 2a), which could be distinguished by naked eyes, suggesting the production of PDI radical anions. UV-Vis spectroscopy provided a quantitative evidence. The characteristic absorption bands of PDI peaked at 500 nm and 540 nm decreased while the characteristic absorption bands of PDI radical anions peaked at 732 nm and 819 nm appeared (Figure S2). Therefore, it was convinced that the reduction of BPDI with $Na_2S_2O_4$ could produce PDI radical anions. At the same concentration, BPDI/$(CB[7])_2$ solution could generate a significantly large amount of PDI radical anions after the same treatment. As shown in Figure 2b, the color of the reduced BPDI/$(CB[7])_2$ solution was dark purple—much darker than BPDI itself. Accordingly, the characteristic absorption of PDI radical anions also appeared in the similar region but with a clear increase in the absorbance (Figure 2c), indicating that the generated PDI radical anions in the BPDI/$(CB[7])_2$ solution are twice as BPDI alone.

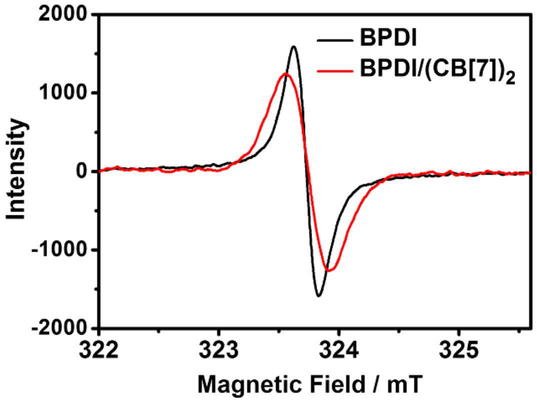


Figure 3. EPR spectra of the radical anions generated from BPDI (0.3 mM) or BPDI/$(CB[7])_2$ (0.3 mM).

	BPDI Radical anion	BPDI/$(CB[7])_2$ Radical anion
g-factor	2.0035	2.0035
Integration	14.7	30.3
Radical anion concentration (mM)	0.016	0.033

Table 1. Detailed EPR signal parameters and radical anion concentrations calculated from the integration.

In order to provide direct evidence for the formation of PDI radical anions, electron paramagnetic resonance (EPR) spectroscopy was also measured for the two solutions after reduction. As shown in Figure 3, they both displayed a typical EPR signal, proving the existence of free radicals. Upon further analysis of the EPR signals, some important parameters could be obtained (Table 1). The *g*-factor of BPDI and BPDI/$(CB[7])_2$ radical anions were both found to be g = 2.0035, which is consistent with the previously reported values[8a, 12], confirming the formation of PDI radical anions. The same *g* values indicate that the two radical anions have similar structures. The integration of EPR signals were calculated to be 14.7 for BPDI radical anions and 30.3 for BPDI/(CB[7])$_2$ radical anions, respectively. Through the EPR standard curve (Figure S4), the concentration of BPDI radical anion was determined to be 0.016 mM, and BPDI/(CB[7])$_2$ radical anion was 0.033 mM. Therefore, the concentration of BPDI/(CB[7])$_2$ radical anion is twice as that of BPDI radical anion, which is consistent with the above UV-Vis data.

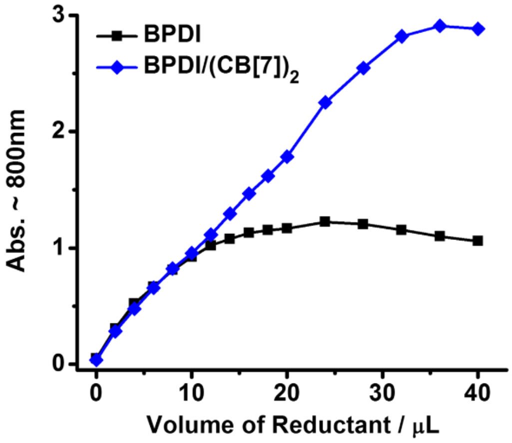


Figure 4. The changing amount of generated radical anions with increasing reductant (BPDI or BPDI/(CB[7])$_2$ solution (0.3 mM, 2 mL) was reduced by 30 mM Na$_2$S$_2$O$_4$ solution).

To comprehensively compare the free radical yield, the reduction titration with gradually adding reductant into BPDI or BPDI/(CB[7])$_2$ solution was performed, monitored with UV-Vis spectroscopy. The absorbance of the characteristic band around 800 nm, which could reflect the amount of generated radical anions in this process, was plotted versus the volume of the Na$_2$S$_2$O$_4$ solution. As exhibited in Figure 4, at the beginning of the titration, only a small amount of radical anion was produced, and the low radical concentration was not favorable to the dimerization and quenching of radical anions, thus the free radical yields of the two solutions were nearly identical because the steric effect of CB[7] was not significant at such a low concentration. However, with increasing dosage of reductant, the concentration of radical anions rose gradually and two samples performed very differently. BPDI radical anions were easy to get closed and dimerized at higher concentrations,[7a, 13] causing the stagnation of increase of the absorbance. While in the BPDI/(CB[7])$_2$ solution, the bulky CB[7] hindered the aggregation of the adjacent radical anions. Consequently the free radical yield in the BPDI/(CB[7])$_2$ solution continued to rise. Therefore, the steric hindrance of CB[7] blocks is critical to the improved free radical yield of supramolecular free radicals.

To further understand the mechanism of improved free radical yield, we reduced the two solutions at different concentrations and then measured the free radical yield monitored with UV-Vis spectroscopy. As shown in Figure 5, the maximal free radical yields in the two solutions both increased with the increasing concentration, as a consequence of the increase of PDI moieties. Remarkably, with the increase of concentration, the maximal yield of BPDI/(CB[7])$_2$ supramolecular free radical increased much faster than BPDI radical anion, which could also be revealed by calculating the improvement ratio of BPDI/(CB[7])$_2$ supramolecular free radical yield against BPDI radical anion (Figure S6). As mentioned above, after the formation of the supramolecular complex, the bulky CB[7] heads can suppress the aggregation of BPDI. Therefore, at the higher concentration, as a result of the more intense aggregation of BPDI, the deaggregating effect of CB[7] is more significant, inducing a greater improvement of free radical yield. This phenomenon further supports the mechanism described above.

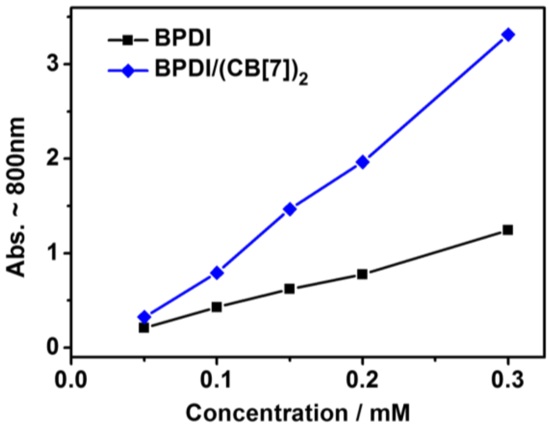


Figure 5. The maximal free radical yields (monitored with UV-Vis) in BPDI and BPDI/(CB[7])$_2$ solutions at different concentrations. The series of concentrations are 0.05, 0.1, 0.15, 0.2, 0.3 mM.

So far we have fabricated the BPDI/(CB[7])$_2$ supramolecular free radicals and improved PDI free radical yield with the help of CB[7] blocks. It is thus anticipated that the supramolecular free radical can attain a more effective NIR photothermal conversion. Hence, we performed photothermal conversion experiments. With 808 nm irradiation at 1 W cm^{-2} and room temperature of 25.1 ℃, the temperature elevation of aqueous solutions containing BPDI radical anions or BPDI/(CB[7])$_2$ radical anions was measured, respectively (Figure 6). The blank test demonstrated that the temperature of pure water only increased by less than 3 ℃ within 10 min. On the other hand, a significant increase of temperature was observed after irradiating BPDI radical anions or BPDI/(CB[7])$_2$ radical anions. It should be noted that the solution containing BPDI/(CB[7])$_2$ supramolecular free radicals had a faster rate as well as more temperature increase than BPDI radical anions. Within 10 min, the temperature of the BPDI solution increased by 9.4 ℃, whereas the BPDI/(CB[7])$_2$ solution increased by 19.5 ℃. Thus, the 808 nm laser heat conversion efficiency was determined to be 16.3% for BPDI radical anions and 31.6% for BPDI/(CB[7])$_2$ radical anions, according to the modified calculation method used for photothermal conversion efficiency by Roper et al[14] (see Figure S7 and Table S1 in the Supporting Information). It is evident that the NIR photothermal conversion efficiency of the supramolecular free radicals has been enhanced by approximately 94% compared to that of their building blocks.

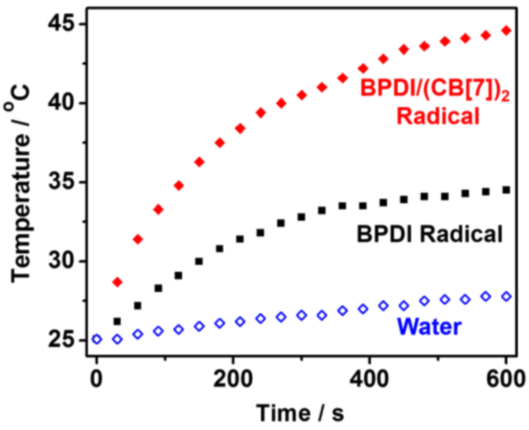


Figure 6. Photothermal conversion experimental data: Temperature elevation of aqueous solutions containing BPDI radical anions or BPDI/(CB[7])$_2$ radical anions as a function of time (0 – 600 s) under irradiation with a 808 nm laser at a power density of 1.00 W cm^{-2}. Pure water was the blank control.

In addition to the facile fabrication of such supramolecular strategy, one more advantage of supramolecular free radicals is the reversibility inheriting from the dynamic host–guest interactions. 1-Adamantanamine hydrochloride (AD), which has a binding constant as high as 4.2×10^{12} M^{-1} with CB[7],[9d] was added into the BPDI/(CB[7])$_2$ supramolecular complex. The preferred binding of CB[7] to the AD guest could lead to the dissociation of the BPDI/(CB[7])$_2$ supramolecular complex and the recovery of the close stacking of PDI aromatic cores, as confirmed by ^{1}H NMR, UV-Vis and fluorescence spectroscopy (Figure S8). The spectra of BPDI/(CB[7])$_2$/AD$_{2.5}$ were nearly the same as BPDI itself. In addition, the radical anions generated in BPDI/(CB[7])$_2$/AD$_{2.5}$ solution also recovered to the initial quenched state without the assistance of CB[7] heads (Figure S8). All the above results have revealed that the supramolecular free radicals are highly reversible and adaptive.

Conclusions

In summary, we have successfully fabricated a novel kind of supramolecular free radical with significantly improved free radical yield and NIR photothermal conversion efficiency. The fabrication of the supramolecular free radical is based on host-guest interactions, which is facile, reversible and highly efficient. The supramolecular free radical has an improved photothermal conversion efficiency (31.6%) comparable to commercial gold nanorods (~22%),[1c, 1d] which is one of the most widely known photothermal systems. Furthermore, the dynamic and adaptive properties derived from supramolecular interactions exhibit the potential for the construction of smart materials. We anticipate that such supramolecular approach can be extended to other aromatic free radicals, and supramolecular free radicals with enhanced photothermal conversion may open access to applications in photothermal therapy and light-triggered drug release.

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Notes and references

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