

### Photoresponsive Materials

How to cite:

International Edition: doi.org/10.1002/anie.202103125 German Edition: doi.org/10.1002/ange.202103125

### Single-Photon Near-Infrared-Responsiveness from the Molecular to the Supramolecular Level via Platination of Pentacenes

Yifei Han, Yueru Yin, Fan Wang, and Feng Wang\*

Abstract: Near-infrared (NIR) responsiveness is important for various applications. Currently, single-photon NIR-responsive systems are rare compared to systems that display two-photon absorption and triplet-triplet annihilation processes. Supramolecular stacking of photo-responsive chromophores results in decreased efficiency due to space-confinement effects. Herein we show that  $\sigma$ -platination of pentacenes is a feasible protocol to build single-photon NIR-responsive systems, with advantages including a low HOMO-LUMO energy gap, high photochemical efficiency, and pathway specificity. The pentacene-to-endoperoxidation transformation is accompanied by color and absorbance changes. The high photo-oxygenation efficiency of  $\sigma$ -platinated pentacenes facilitates NIR responsiveness in one-dimensional supramolecular polymers, resulting in the disappearance of supramolecular chirality signals and disruption of self-assembled nanofibers. Overall, the  $\sigma$ platination strategy opens up new avenues toward NIR photoresponsive materials at the molecular and supramolecular levels.

#### Introduction

Light-responsive systems have been constructed on the basis of azobenzenes, coumarins, spiropyrans, cinnamates, etc.<sup>[1]</sup> However, these compounds are triggered by UV and high energy visible lights, which inevitably bring photodamage issues. We sought to develop photo-responsive systems by near-infrared (NIR) light. For UV/Vis photoresponsive compounds, NIR photosensitization was achieved by two-photon absorption (TPA),<sup>[2a]</sup> triplet-triplet annihilation (TTA-UC),<sup>[2b,c]</sup> or lanthanide-doped upconverting nanoparticles (UCNPs).<sup>[2d,e]</sup> These approaches still suffer from some problems: TPA needs high excitation power density (typical pulse intensity for the ultrafast laser:  $> 10^6 \,\mathrm{W \, cm^{-2}}$ ), while TTA-UC and UCNPs require the participation of NIRabsorbing agents. It is intriguing to develop new photosensitive chromophores, which respond to NIR light via normal single-photon absorption.<sup>[3]</sup> Another issue is the decreased efficiency of photo-responsive compound upon supramolecular stacking.<sup>[4]</sup> Van Esch reported the blocking of

[\*] Y. Han, Y. Yin, F. Wang, Prof. Dr. F. Wang CAS Key Laboratory of Soft Matter Chemistry Department of Polymer Science and Engineering University of Science and Technology of China Hefei, Anhui 230026 (P. R. China) E-mail: drfwang@ustc.edu.cn

 Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202103125. photochemical *trans-cis* isomerization for azobenzene derivatives in supramolecular gels due to a space confining effect.<sup>[4a]</sup> Hence, effective single-photon NIR-responsive systems achieved at molecular and supramolecular levels remain challenging.

Pentacene has been extensively studied for its photoreactivity,<sup>[5]</sup> yet rarely employed as a programmable photoresponsive chromophore. The low solubility of pentacene restricts photo-chemical operability in organic solvents.<sup>[6]</sup> Pathway complexity (photo-oxidation by singlet oxygen, versus photo-dimerization)<sup>[5]</sup> brings poor structural specificity for the photo-irradiated products. Linker's and Thomas's groups have addressed these issues, by attaching bulky alkylsilyl<sup>[7]</sup> or phenyl<sup>[8]</sup> substituents on the zig-zag edges of pentacenes (compound **3**, Scheme 1). Nevertheless, these pentacenes exhibit visible light rather than NIR responsiveness. Self-assembly of such pentacenes into ordered supramolecular nanostructures has been rarely explored, due to the difficulty for further chemical derivatization.

Here, effective NIR photo-responsive systems have been constructed at molecular and supramolecular levels, by coordinating pentacenes to form  $\sigma$ -platinated complexes.<sup>[9]</sup> For compound 1 (Scheme 1),  $\sigma$ -platination reduces the HOMO-LUMO gap through interplay between Pt<sup>II</sup> 5dorbitals and dialkynylpentacene ligand orbitals. It guarantees red-shifting of the absorption and tails in the NIR region. The Pt<sup>II</sup>(PBu<sub>3</sub>)<sub>2</sub> units prevent packing of pentacenes, which improves solubility of 1 and favors photo-oxygenation over photo-dimerization. NIR irradiation of 1 transforms pentacene into its endoperoxide with color changes (Scheme 1). The architectural template effect<sup>[10]</sup> of Pt<sup>II</sup> ions facilitates the design of supramolecular monomer 2 via the acetylene linkage (Scheme 1). One-dimensional supramolecular polymerization takes place for 2 in apolar media, due to intermolecular hydrogen bonds of the amide units (Scheme 1).<sup>[11]</sup> Photo-oxygenation proceeds in the supramolecular stacks of 2, which disrupts self-assembled nanofibers and decreases supramolecular chirality signals upon NIR irradiation.

#### **Results and Discussion**

**Spectroscopy of σ-platinated pentacene 1.** Compound **1** exhibited four absorption bands in CHCl<sub>3</sub> (Figure S1b): a very strong absorption at 286–333 nm, a shoulder band at 335–402 nm, a narrow band at 427–450 nm, and low-energy vibronic bands reaching into NIR region  $[\lambda_{max}: 686 \text{ nm } (\varepsilon = 3.28 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1})$ , 630 nm  $(\varepsilon = 1.79 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1})$ , 583 nm  $(\varepsilon = 5.80 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1})$ , Figure 1a]. The low-

Wiley Online Library

© 2021 Wiley-VCH GmbH

Angew. Chem. Int. Ed. 2021, 60, 2-9

These are not the final page numbers!



Scheme 1. Schematic representation for NIR photo-responsiveness of pentacene derivatives 1-2 at both molecular and supramolecular levels.

energy bands were  $\approx 40$  nm red-shifted compared to those of TIPS-substituted pentacene **3** ( $\lambda_{max}$ : 642 nm, 591 nm, 549 nm, TIPS = triisopropylsilyl, Figure 1 a). According to DFT calculations,<sup>[12]</sup> the HOMO energy was -4.165 eV for **1** (Figure 1b), destabilized than that of **3** (HOMO: -4.610 eV, Figure 1b). Meanwhile, the LUMO energy levels were -2.316 eV for **1** and -2.710 eV for **3** (Figure 1b). [Pt-(PBu<sub>3</sub>)<sub>2</sub>I]<sup>+</sup> perturbs the HOMOs than the LUMOs, due to higher energy matching between the HOMO of 6,13-dialky-nylpentacene and the 5*d* orbital of Pt<sup>II</sup> centers.<sup>[9b,c]</sup> The calculated HOMO-LUMO gap decreased from **3** (1.90 eV, 652 nm) to **1** (1.85 eV, 670 nm), consistent with the experimental results.

According to the DFT calculations of **1**, the electron densities of HOMO and LUMO orbitals were primarily distributed over the dialkynylpentacene unit, with minor contribution from Pt<sup>II</sup> ions (Figure 1b). The NIR absorbance of **1** belongs to the electronic transition of Pt<sup>II</sup>-perturbed dialkynylpentacene. Time-dependent density functional theory (TDDFT)<sup>[12]</sup> (Figures S2-S3) indicated the broad absorption band of **1** centered at 791 nm to be the HOMO to LUMO transitions (composition: 100%, Table S1 and Figure S2), with an oscillator strength value (*f*) of 0.292. By contrast, for the simulated UV/Vis spectrum of **3**, the HOMO–LUMO transition (composition: 100%, Table S1 and Figure S3) was located at 762 nm (*f*: 0.225). Evidently,  $\sigma$ -platination gave rise

to bathochromic HOMO-LUMO shifts of the pentacene units.

Endoperoxidation of σ-platinated pentacene via NIR irradiation. The low-energy HOMO -> LUMO transition of 1 stimulated us to investigate its NIR-responsive behaviors. Upon irradiation of 1 ( $c = 1.0 \times 10^{-5}$  M in CHCl<sub>3</sub>) with 680 nm light-emitting-diode (LED) lamp (intensity: 32.8 mW cm<sup>-2</sup>), the low-energy transitions within 500-740 nm declined for the intensities (Figure 2a), accompanied by color change from cyan to colorless (Figure 2a, inset). The results suggested structural disruption of the 6,13-dialkynylpentacene moiety on 1, as further evidenced by <sup>1</sup>H NMR experiments [Figure 2c, (i) and (ii)]. Upon 680 nm photo-irradiation, the pentacene resonances vanished ( $\delta$ : 9.31 ppm for H<sub>a</sub>, 7.89 ppm for  $H_{\rm b}$ , and 7.31 ppm for  $H_{\rm c}$ ), accompanied by the emergence of a new set of resonances ( $\delta$ : 8.25 ppm for H<sub>a'</sub>, 7.81 ppm for  $H_{b'}$ , and 7.47 ppm for  $H_{c'}$ ). In view of the symmetrical splitting patterns of the final product, two possible photo-chemical reactions might take place, namely [4+4] dimerization or [4+2] endoperoxidation of the pentacene unit.

The photo-irradiated product was clarified. Upon purging nitrogen into chloroform solution of **1**, the absorbance hardly changed upon light irradiation (Figure S4). DFT computations revealed nearly perpendicular arrangement between  $Pt(PBu_3)_2$  and pentacene units on **1**, thus preventing orbital overlapping between the neighboring molecules (Figure S5a).

© 2021 Wiley-VCH GmbH



**Figure 1.** a) Absorption spectra of 1 and 3 (c=0.01 mM in chloroform) in the visible/NIR region. b) FMO energy levels and the corresponding electron densities (isovalue=0.02) of compounds 3, 1, and 1-O<sub>2</sub>. The black lines and red lines mark the energy levels of HOMOs and LUMOs, respectively.

Hence, it precluded the feasibility of [4+4] photo-dimerization. For photo-irradiated endoperoxidation of **1** (Scheme 1), the participation of O<sub>2</sub> was validated by using 9,10-dimethylanthracene (DMA) as the singlet oxygen ( $^{1}O_{2}$ ) capturer. For the mixture of DMA and **1** in chloroform, the absorption band of DMA (334–427 nm) declined upon 680 nm irradiation (Figure S6a). The phenomenon was ascribed to energy transfer between the excited state of **1** and O<sub>2</sub> to generate  $^{1}O_{2}$ (Figure S6c,d), which reacts with DMA to provide DMA-O<sub>2</sub>.<sup>[13]</sup> Upon heating the endoperoxide **1**-O<sub>2</sub> at 60°C under inert atmosphere for 18 hours, the pentacene <sup>1</sup>H NMR resonances reappeared (Figure 2c, iii). Simultaneously, a *m*/ *z* signal at 1776.5554 was present in the MALDI-TOF spectrum (Figure S11), indicating the reversible endoperoxide-to-pentacene transition upon thermolysis.

Mechanism for the [4+2] endoperoxidation reaction of **1** was elucidated via theoretical calculations. The Gibbs free energies (G) of **1**, **1**-O<sub>2</sub> and <sup>1</sup>O<sub>2</sub> were calculated to be -4517.293325 a.u., -4667.611739 a.u. and -150.272626 a.u., respectively. The Gibbs free energy change ( $\Delta G$ ) value for photo-oxygenation was calculated to be -0.0458 a.u. (corresponding to -120.2 kJ mol<sup>-1</sup>), higher than that of **3** (-0.0362 a.u., corresponding to -95.1 kJ mol<sup>-1</sup>). The results demonstrated thermodynamically favorable photo-oxygenation of pentacenes upon  $\sigma$ -platination. DFT calculations also explained the vanishing of NIR absorbance upon [4+2] photo-oxygenation: **1**-O<sub>2</sub> displayed higher HOMO–LUMO gap than that of **1** (4.10 eV versus 1.85 eV, Figure 1b). It



**Figure 2.** a) Time-dependent absorbance decay of 1 ( $c = 1.0 \times 10^{-5}$  M) in CHCl<sub>3</sub> upon photo-irradiation at 680 nm (intensity: 32.8 mWcm<sup>-2</sup>). b) Kinetics for the [4+2] photo-oxygenation of 1 and 3 in chloroform under photo-irradiation at 680 nm and 730 nm (intensity: 30.4 mWcm<sup>-2</sup>). c) Pentacene-to-endoperoxide conversion of 1 characterized by <sup>1</sup>H NMR experiments (c = 4.0 mM in CDCl<sub>3</sub>): (i) prior to photo-irradiation; (ii) after photo-irradiation at 680 nm, and (iii) after deoxygenation upon heating at 60°C in nitrogen atmosphere for 18 hours.

originated from the discrepancies of transition compositions for the two compounds. In detail, HOMO–LUMO of  $1-O_2$ arose from the admixtures of LLCT (from I<sup>-</sup> and C=C units to endoperoxidized pentacene) and MLCT (from Pt<sup>2+</sup> to endoperoxidized pentacene) transitions (Figure 1b), which were different form metal-perturbed  $\pi \rightarrow \pi^*$  transitions of **1**.

On this basis, the photo-oxygenation kinetics of 1 were exploited, by monitoring the absorbance intensities at 680 nm versus the irradiation time. As shown in Figure 2b, the absorbance decay conformed to pseudo-first-order kinetics, with an observed photo-oxygenation rate constant  $(k_{obs})$  of 0.114 min<sup>-1</sup> [photochemical quantum yield ( $\Phi$ ): 0.0173% at the light intensity of  $32.8 \text{ mW cm}^{-2}$ , Figure S7a]. The  $k_{obs}$ value of **1** was 23-fold higher than that of **3**  $(0.005 \text{ min}^{-1})$ , Figure 2b). In addition, 730 nm LED lamp was employed as the NIR light source. The conversion from 1 to  $1-O_2$ proceeded upon 730 nm light irradiation (intensity: 30.4 mW cm<sup>-2</sup>), with a much higher  $k_{obs}$  value than that of **3**  $(0.011 \text{ min}^{-1} \text{ versus } 0.0002 \text{ min}^{-1}, \text{ Figure 2 b})$ . These results were attributed to the lower HOMO-LUMO gap of 1 than 3, leading to higher molar absorption coefficient in the NIR region.

Effect of  $\sigma$ -platination on photo-oxygenation regioselectivity. Photo-irradiation of 1 displayed not only pathway specificity, but high regioselectivity at the 6,13-positions (the

www.angewandte.org

alkynylated positions of pentacene). According to the frontier molecular orbital (FMO) theory, the second-order perturbation energy ( $\Delta E$ ) reflects orbital overlapping between the "termini" of acene rings and  ${}^{1}O_{2}$ .<sup>[5d,e]</sup> To achieve the highest  $\Delta E$  value [Eq. (S1)],  ${}^{1}O_{2}$  adducted to aromatic rings with the largest coefficients for the atom orbitals.<sup>[5b,d,e,7a]</sup> For **1**, the largest orbital coefficients located at the innermost ring (0.410 and -0.404 for 6,13-positions, Figure 3 a), which were larger those of **3** (0.397 and -0.397, Figure 3 a).



Figure 3. Calculated atom orbital coefficients for the HOMOs (isovalue=0.02) of a) pentacene-based compounds 1 and 3, together with b) TIPS-substituted tetracene 4 and  $\sigma$ -platinated tetracene 5. All hydrogen atoms in FMOs are omitted for clarity.

For tetracene derivatives, poor [4+2] photo-oxygenation regioselectivity existed.<sup>[7a, 8c]</sup> For example, two regioisomers (5,12- and 6,11- positions) were obtained in 1:2 mole ratio upon light irradiation of TIPS-substituted tetracene 4 (Figure 3b and Figure S9a). We sought to investigate  $\sigma$ -platination effect on [4+2] endoperoxidation regioselectivity of tetracenes. The  $\sigma$ -platinated tetracene 5 (Figure 3b) favored for the formation of 5,12-regioisomer (mole ratio of 5,12- and 6,11-regioisomers: 8.5:1, Figures S9,S10). The improved [4+2] photo-oxygenation regioselectivity for 5 over 4 was elucidated via the FMO theory (Figure 3b). For 4, the orbital coefficients of 5,12-positions were 0.401 and -0.401, while comparable values were obtained for the 6,11-positions (0.369 and -0.369, respectively). Upon  $\sigma$ -platination, the orbital coefficients for 5,12-positions displayed negligible changes (0.409 and -0.403 for 5). In contrast, the 6,11-positions were greatly perturbed, as manifested by the decrease of orbital coefficients (0.310 and -0.313 for 5 versus 0.369 and -0.369for 4). Both experimental and computational results demonstrated the improvement of [4+2] photo-oxygenation regioselectivity via σ-platination of high-order acenes.

Supramolecular polymerization of  $\sigma$ -platinated pentacene 2. NIR photo-responsiveness was further amplified at the supramolecular level, by incorporating  $\sigma$ -platinated pentacene into the structure of **2**. To ensure supramolecular polymerization of **2**, less bulky PEt<sub>3</sub> units (Figure S13) were introduced on the monomer structure instead of PBu<sub>3</sub> units in **1.** Two amides were attached on both sides of  $\sigma$ -platinated pentacene, which reinforced packing capability via the participation of intermolecular hydrogen bonds. In apolar methylcyclohexane (MCH, c = 0.02 mM), the maximal  $\pi \rightarrow \pi^*$ absorbance of **2** located at 685 nm, with the presence of four isosbestic points (588 nm, 636 nm, 656 nm, and 698 nm) upon varying the temperature (Figure S14). The results indicated the transition from monomeric to self-assembled states upon lowering the temperature.

As widely documented, circular dichroism (CD) spectroscopy is a powerful tool to study supramolecular polymerization properties, since supramolecular chirality signals are present for long-range ordered chiral assemblies yet absent for monomers and oligomers.<sup>[14]</sup> To induce helical bias for 2, optically active (S)-3,7-dimethyloctyl groups were introduced to the peripheral side chains. At 60 °C, no bisignate CD signal was detected for 2 in MCH, indicating the dominance of molecularly dissolved state (Figure 4a). In stark contrast, strong bisignate Cotton effect existed at 5°C (Figure 4a), with the positive maximum at 320 nm ( $\Delta \varepsilon = 203 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ) and the negative one at 332 nm ( $\Delta \varepsilon = -112 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ). It demonstrated the formation of helical supramolecular polymers at low temperature. Supramolecular chirality signals also emerged in the NIR region ( $\Delta \varepsilon = -18.2 \text{ Lmol}^{-1} \text{ cm}^{-1}$  at 705 nm, Figure 4a, inset), ascribed to chirality transfer from the peripheral alkyl chains to the inner  $\sigma$ -platinated pentacene core. Such low-energy CD signals have been seldom encountered in the previous helical supramolecular systems.[15]

By monitoring CD intensities at 319 nm versus temperature (melting rate:  $60 \,^{\circ} \mathrm{Ch}^{-1}$ ), a non-sigmoidal melting curve was obtained for **2**, with the critical temperature point ( $T_{\rm e}$ ) at 25 °C (Figure 4b). Hence, **2** assembled into supramolecular polymers in MCH via the cooperative nucleation-elongation mechanism.<sup>[16]</sup> The thermodynamic parameters for supramolecular polymerization processes were acquired via the van't Hoff plot (Figure 4c, and Figure S16). The enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) values were determined to be -62.8 kJ mol<sup>-1</sup> and -121 J mol<sup>-1</sup>K<sup>-1</sup>, respectively, suggesting the enthalpy-driven process for supramolecular polymerization of **2**.

The supramolecular polymerization mechanism was clarified via DFT computations.<sup>[12]</sup> In the optimized geometry of the dimeric stacks  $2_2$  (Figure 4d), the dihedral angles between PEt<sub>3</sub> ligands and pentacene unit are reduced (33.4–44.7°) compared to those of 2 (dihedral angel: 92.4° and 105.0°, Figure S5c). Pt(PEt<sub>3</sub>)<sub>2</sub> moieties on the same side of  $2_2$  adopt the identical twisting directions, giving rise to the rotation angle of 4.4° for the neighbouring monomers. As a result, steric hindrance is decreased for the dimeric stacked structure  $2_2$ . The N-H-O distances are 1.85 Å and 1.91 Å for the neighbouring amides (Figure 4d), suggesting that intermolecular hydrogen bonds constitute the primary driving forces for supramolecular polymerization of 2. The conclusion is demonstrated by <sup>1</sup>H NMR measurements, with downfield shifts of the amide resonances upon increasing the monomer concentration (from 7.65 ppm at 2.00 mM to 7.81 ppm at 43.5 mM in CDCl<sub>3</sub>, Figure S17). The pentacene-pentacene



*Figure 4.* a) CD spectra of **2** (c=0.02 mM in MCH) at two different temperatures (inset: magnified CD spectra for the NIR absorption region). b) Non-sigmoidal melting curve of **2** (c=0.02 mM) in MCH. c) Van't Hoff plot analysis for the supramolecular polymerization process. d) Optimized geometries for **2**<sub>2</sub>: top view (top, hydrogen atoms are omitted for clarity) and side view (bottom).

distance ranges from 3.46 Å to 7.73 Å in  $\mathbf{2}_2$  (Figure 4d), suggesting that  $\pi$ - $\pi$  stacking interactions might also participate in the supramolecular polymerization process.

NIR responsiveness of chiral supramolecular polymers. Upon 680 nm or 730 nm photo-irradiation, the solution color of 2 varied from green to pale yellow in MCH (Figure 5a, inset). Simultaneously, the bisignate CD signals disappeared (Figure 5a). The phenomena illustrated NIR responsiveness of chiral supramolecular polymers derived from 2. We rationalized that 2 underwent photo-oxygenation during NIR irradiation, with large steric hindrance for the nonplanar endoperoxide  $2-O_2$  (Scheme 1). It failed to stack with each other, and led to the breakup of one-dimensional selfassembled polymers with the decrease of supramolecular chirality signals. The conclusion was evidenced by atomic force microscopy (AFM) characterizations. As shown in Figure 5c, self-assembled helical nanofibers with micrometer length formed for 2, which tended to intertwine with each other. These nanofibers totally vanished upon NIR light irradiation (Figure 5d). Small-angle X-ray scattering (SAXS) of **2** exhibited the *d*-spacing values of  $1:1/\sqrt{3.45}:1/\sqrt{5.45}$ . The periodic ordering also disappeared upon NIR light irradiation (Figure 5b). Hence, NIR-triggered disruption of long-range ordered nanostructures occurred for 2.

Supramolecular polymers are described by dynamic equilibria between monomeric and aggregated state.<sup>[17]</sup> Considering the strong supramolecular polymerization tendency of **2**, the amount of monomeric species was trivial in apolar

media (for 0.02 mM of **2** in MCH at 10 °C, the free monomeric species was calculated to be  $9.48 \times 10^{-11} \text{ mol } \text{L}^{-1}$ , Equations



**Figure 5.** a) Changes in the CD spectra of supramolecular polymers derived from 2 (c=0.02 mM in MCH) upon 680 nm light irradiation (intensity: 64.2 mWcm<sup>-2</sup>). b) SAXS spectra of supramolecular polymers derived from 2 [c=25 mM in MCH/CHCl<sub>3</sub>=90/10 ( $\nu/\nu$ )] before and after 680 nm light irradiation. AFM height images of 2 (5  $\mu$ M of 2 in MCH drop-cast on mica) c) before and d) after 680 nm light irradiation.

These are not the final page numbers!

© 2021 Wiley-VCH GmbH

S10–S16). It can be concluded that supramolecular polymers participated in the photo-oxygenation process in MCH. The  $k_{\rm obs}$  values for pentacene-to-endoperoxide transition were determined to be 0.056 min<sup>-1</sup> upon 680 nm irradiation ( $\Phi$ : 0.0118% for supramolecular polymeric state versus 0.0342% for monomeric state with the light intensity of 64.2 mW cm<sup>-2</sup>, Figure S18), and 0.0126 min<sup>-1</sup> upon 730 nm irradiation (Figures S19). Although the  $k_{\rm obs}$  values were lower than those obtained in the monomeric states ( $k_{\rm obs}$ : 0.144 min<sup>-1</sup> upon 680 nm irradiation, Figures S18,S19), the current system still represented a rare example of NIR-responsive supramolecular polymeric systems.

As previously documented, photo-responsiveness was inhibited when azobenzenes stacked with each other in supramolecular assemblies.<sup>[4]</sup> We envisaged that, unlike photo-isomerization encountered in azobenzenes, small conformational change took place for  $\sigma$ -platinated pentacene during the photo-oxygenation process (the angle change between Pt<sup>II</sup> ions and 6,13-positions of pentacene units was calculated to be 12.0°, Figure S21). In addition,  $\sigma$ -platination prevented close  $\pi$ - $\pi$  packing of pentacenes (DFT calculation: 3.46 Å–7.73 Å, Figure 4d), facilitating the diffusion of  ${}^{1}O_{2}$  into supramolecular polymers. Therefore, the space confining effect exerted minor effect on photo-chemical transition, which in turn enhanced photo-responsive efficiency at supramolecular level.

#### Conclusion

In summary,  $\sigma$ -platinated pentacenes 1 and 2 represent novel single-photon NIR-responsive systems at molecular and supramolecular levels. The platination strategy brings a great number of advantages to the parent pentacenes, including greater solubility, bathochromic shift to NIR absorbance, high photochemical efficiency, and pathway specificity. It facilitates the transformation from the cyancolored pentacene form to colorless [4+2] endoperoxide upon NIR light irradiation. NIR responsiveness further takes place for supramolecular polymers from 2, accompanied by a decrease in supramolecular chirality signals and disruption of self-assembled nanofibers. It overcomes the space-confinement effects encountered in the conventional light-responsive supramolecular stacks. Overall, the current study opens up new avenues toward NIR photo-responsive materials with tailored functionalities.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (21922110, 21871245, and 21674106), and the Fundamental Research Funds for the Central Universities (WK345000005). All DFT and TDDFT computations of this manuscript have been performed on the supercomputing center. We are grateful for the technical support from the High Performance Computing Center of University of Science and Technology of China.

#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** metalloligands · photoresponsive materials · polycyclic aromatic hydrocarbons · self-assembly · supramolecular polymers

- a) A. Goulet-Hanssens, F. Eisenreich, S. Hecht, Adv. Mater.
   2020, 32, 1905966; b) Z. L. Pianowski, Chem. Eur. J. 2019, 25, 5128-5144; c) L. Wang, Q. Li, Chem. Soc. Rev. 2018, 47, 1044– 1097; d) E. R. Draper, D. J. Adams, Chem. Commun. 2016, 52, 8196-8206; e) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 2014, 114, 12174-12277; f) D. Villarón, S. J. Wezenberg, Angew. Chem. Int. Ed. 2020, 59, 13192-13202; Angew. Chem. 2020, 132, 13292-13302; g) D. Roke, C. Stuckhardt, W. Danowski, S. J. Wezenberg, B. L. Feringa, Angew. Chem. Int. Ed. 2018, 57, 10515-10519; Angew. Chem. 2018, 130, 10675-10679.
- [2] a) K. Mutoh, Y. Kobayashi, T. Yamane, T. Ikezawa, J. Abe, J. Am. Chem. Soc. 2017, 139, 4452-4461; b) A. Tokunaga, L. M. Uriarte, K. Mutoh, E. Fron, J. Hofkens, M. Sliwa, J. Abe, J. Am. Chem. Soc. 2019, 141, 17744-17753; c) Z. Jiang, M. Xu, F. Li, Y. Yu, J. Am. Chem. Soc. 2013, 135, 16446-16453; d) W. Yu, L. Yao, T. Yang, R. Yin, F. Li, Y. Yu, J. Am. Chem. Soc. 2011, 133, 15810-15813; e) J.-C. Boyer, C.-J. Carling, B. D. Gates, N. R. Branda, J. Am. Chem. Soc. 2010, 132, 15766-15772.
- [3] a) K. Klaue, W. Han, P. Liesfeld, F. Berger, Y. Garmshausen, S. Hecht, J. Am. Chem. Soc. 2020, 142, 11857-11864; b) P. Lentes, E. Stadler, F. Röhricht, A. Brahms, J. Gröbner, F. D. Sönnichsen, G. Gescheidt, R. Herges, J. Am. Chem. Soc. 2019, 141, 13592-13600; c) J. R. Hemmer, S. O. Poelma, N. Treat, Z. A. Page, N. D. Dolinski, Y. J. Diaz, W. Tomlinson, K. D. Clark, J. P. Hooper, C. Hawker, J. Read de Alaniz, J. Am. Chem. Soc. 2016, 138, 13960-13966; d) M. Dong, A. Babalhavaeji, C. V. Collins, K. Jarrah, O. Sadovski, Q. Dai, G. A. Woolley, J. Am. Chem. Soc. 2017, 139, 13483-13486.
- [4] a) S. van der Laan, B. L. Feringa, M. Kellogg, J. van Esch, Langmuir 2002, 18, 7136–7140; b) X.-D. Xu, J. Zhang, L.-J. Chen, X.-L. Zhao, D.-X. Wang, H.-B. Yang, Chem. Eur. J. 2012, 18, 1659–1667; c) M. Akazawa, K. Uchida, J. J. D. de Jong, J. Areephong, M. Stuart, G. Caroli, W. R. Browne, B. L. Feringa, Org. Biomol. Chem. 2008, 6, 1544–1547.
- [5] a) S. Dong, A. Ong, C. Chi, J. Photochem. Photobiol. C 2019, 38, 27–46; b) A. R. Reddy, M. Bendikov, Chem. Commun. 2006, 1179–1181; c) J.-M. Aubry, C. Pierlot, J. Rigaudy, R. Schmidt, Acc. Chem. Res. 2003, 36, 668–675; d) S.-H. Chien, M.-F. Cheng, K.-C. Lau, W.-K. Li, J. Phys. Chem. A 2005, 109, 7509–7518; e) C. J. M. van den Heuvel, J. W. Verhoeven, T. J. de Boer, Recl. Trav. Chim. Pays-Bas. 1980, 99, 280–284.
- [6] J. E. Anthony, Angew. Chem. Int. Ed. 2008, 47, 452–483; Angew. Chem. 2008, 120, 460–492.
- [7] a) W. Fudickar, T. Linker, J. Am. Chem. Soc. 2012, 134, 15071–15082; b) J. Chen, S. Subramanian, S. R. Parkin, M. Siegler, K. Gallup, C. Haughn, D. C. Martin, J. E. Anthony, J. Mater. Chem. 2008, 18, 1961–1969.
- [8] a) Y. Yan, Z. A. Lamport, I. Kymissis, S. W. Thomas III, J. Org. Chem. 2020, 85, 12731–12739; b) J. Zhang, R. H. Pawle, T. E. Haas, S. W. Thomas III, Chem. Eur. J. 2014, 20, 5880–5884; c) J. Zhang, S. Sarrafpour, T. E. Haas, P. Müller, S. W. Thomas III, J. Mater. Chem. 2012, 22, 6182–6189.
- [9] a) C.-C. Ko, V. W.-W. Yam, Acc. Chem. Res. 2018, 51, 149–159;
  b) M.-H. Nguyen, C.-Y. Wong, J. H. K. Yip, Organometallics 2013, 32, 1620–1629;
  c) M.-H. Nguyen, J. H. K. Yip, Organometallics 2011, 30, 6383–6392;
  d) J. C.-H. Chan, W. H. Lam, H.-L. Wong, N. Zhu, W.-T. Wong, V. W.-W. Yam, J. Am. Chem. Soc.

# These are not the final page numbers!

www.angewandte.org

2011, 133, 12690-12705; e) S. Ibáñez, M. Poyatos, E. Peris, Angew. Chem. Int. Ed. 2018, 57, 16816-16820; Angew. Chem.
2018, 130, 17058-17062; f) S. Ibáñez, E. Peris, Angew. Chem. Int. Ed. 2019, 58, 6693-6697; Angew. Chem. 2019, 131, 6765-6769; g) S. Ibáñez, M. Poyatos, E. Peris, Angew. Chem. Int. Ed. 2017, 56, 9786-9790; Angew. Chem. 2017, 129, 9918-9922; h) Z. Gao, Y. Tian, H.-K. Hsu, Y. Han, Y.-T. Chan, F. Wang, CCS Chem.
2021, 3, 105-115; i) M. Liu, Y. Han, H. Zhong, X. Zhang, F. Wang, Angew. Chem. Int. Ed. 2021, 60, 3498-3503; Angew. Chem. 2021, 133, 3540-3545; j) Z. Li, Y. Han, F. Wang, Nat. Commun. 2019, 10, 3735; k) Z. Li, Y. Han, F. Nie, M. Liu, H. Zhong, F. Wang, Angew. Chem. Int. Ed. 2021, 60, 8212-8219; Angew. Chem. 2021, 133, 8293-8300.

- [10] W.-Y. Wong, C.-L. Ho, Acc. Chem. Res. 2010, 43, 1246-1256.
- [11] a) M. M. J. Smulders, A. P. H. J. Schenning, E. W. Meijer, J. Am. Chem. Soc. 2008, 130, 606-611; b) A. Langenstroer, K. K. Kartha, Y. Dorca, J. Droste, V. Stepanenko, R. Q. Albuquerque, M. R. Hansen, L. Sánchez, G. Fernández, J. Am. Chem. Soc. 2019, 141, 5192-5200; c) I. Herkert, J. Droste, K. K. Kartha, P. A. Korevaar, T. F. A. de Greef, M. R. Hansen, G. Fernández, Angew. Chem. Int. Ed. 2019, 58, 11344-11349; Angew. Chem. 2019, 131, 11466-11471; d) Z. Gao, Y. Han, F. Wang, Nat. Commun. 2018, 9, 3977; e) Y. Han, M. Liu, R. Zhong, Z. Gao, Z. Chen, M. Zhang, F. Wang, Inorg. Chem. 2019, 58, 12407-12414.
- [12] Gaussian 09, Revision D.01, M. J. Frisch, et al. Gaussian, Inc., Wallingford CT, 2013.
- [13] a) X.-F. Zhang, J. Zhu, J. Lumin. 2019, 205, 148–157; b) S. Goswami, R. W. Winkel, E. Alarousu, I. Ghiviriga, O. F. Mohammed, K. S. Schanze, J. Phys. Chem. A 2014, 118, 11735–11743.

- [14] a) C. C. Lee, C. Grenier, E. W. Meijer, A. P. H. J. Schenning, *Chem. Soc. Rev.* 2009, 38, 671–683; b) P. A. Korevaar, C. Schaefer, T. F. A. de Greef, E. W. Meijer, J. Am. Chem. Soc. 2012, 134, 13482–13491; c) A. Sarkar, S. Dhiman, A. Chalishazar, S. J. George, Angew. Chem. Int. Ed. 2017, 56, 13767–13771; Angew. Chem. 2017, 129, 13955–13959; d) S. Dhiman, A. Jain, S. J. George, Angew. Chem. Int. Ed. 2017, 56, 1329–1333; Angew. Chem. 2017, 129, 1349–1353.
- [15] a) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* 2016, *116*, 13752–13990; b) M. Liu, L. Zhang, T. Wang, *Chem. Rev.* 2015, *115*, 7304–7397.
- [16] P. Jonkheijm, P. van der Schoot, A. P. H. J. Schenning, E. W. Meijer, *Science* 2006, *313*, 80–83.
- [17] a) T. F. A. de Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* 2009, 109, 5687-5754; b) L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* 2015, 115, 7196-7239; c) T. Haino, A. Watanabe, T. Hirao, T. Ikeda, *Angew. Chem. Int. Ed.* 2012, 51, 1473-1476; *Angew. Chem.* 2012, 124, 1502-1505; d) K. Nadamoto, K. Maruyama, N. Fujii, T. Ikeda, S.-I. Kihara, T. Haino, *Angew. Chem. Int. Ed.* 2018, 57, 7028-7033; *Angew. Chem.* 2018, 130, 7146-7151; e) N. Nitta, M. Takatsuka, S.-I. Kihara, T. Hirao, T. Haino, *Angew. Chem. Int. Ed.* 2020, 59, 16690-16697; *Angew. Chem.* 2020, 132, 16833-16840; f) S. Guo, Y. Song, Y. He, X.-Y. Hu, L. Wang, *Angew. Chem. Int. Ed.* 2018, 57, 3163-3167; *Angew. Chem.* 2018, 130, 3217-3221.

Manuscript received: March 2, 2021 Accepted manuscript online: April 7, 2021 Version of record online:

www.angewandte.org **K**These are not the final page numbers!



## **Research Articles**



# **Research Articles**

