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ARTICLE

Aggregation-induced emission and aggregation-promoted photochromism of bis(diphenylmethylene)dihydroacenes†

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Reported here is a new class of pure polycyclic hydrocarbon molecules designed by novel aggregation-induced emission (AIE) strategy with unexpected photochromic properties. The restriction of intramolecular motions was found as a comprehensive mechanism for the AIE effect. The photochromism working mechanism study reveals that the photocyclization reaction of *cis*-stilbene, molecular conformation in single crystal and the tetracene backbone should attribute to the unique photo behavior. Particularly, fast responsive, photo-reversible and thermo-irreversible photochromic effect facilitated in solid state open a new field of aggregation-promoted photochromism.

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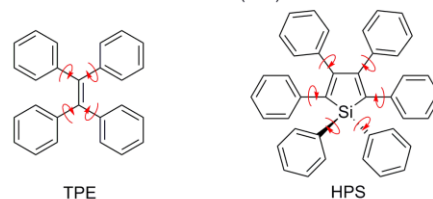
Introduction

Aggregation-induced emission (AIE) refers to a phenomenon that a class of luminogens is molecularly nonemissive but become highly emissive when cluster into aggregates. Luminogenic materials with AIE characteristics have attracted extensive interest and found varied applications.^{1,2} Based on two archetypal AIE luminogens tetraphenylethene (TPE) and hexaphenylsilole (HPS) which contain multiple phenyl peripheries (rotor) linked to the ethylene or silole core (stator) via single bonds (axis), the restriction of intramolecular rotation (RIR) process was proposed as the main cause of the AIE effect (Fig. 1).³ This RIR mechanism has been successfully utilized to explore a large variety of new fluorescent and phosphorescent materials with high luminescent quantum yield in their solid state. However, some newly emerging AIE systems such as the nonplanar THBA⁴ and BCOT⁵ (Fig. 1), which are absent from multiple rotors. As well known, rotation and vibration are the two main modes of molecular motions accompanied by energy consumption. We proposed that the AIE effect of THBA and BCOT maybe mainly originate from the restriction of intramolecular vibrations.⁶ The phenyl rings could be viewed as vibration parts which are connected by a flexible bridge, heptagon for THBA and octagon for BCOT, respectively. Upon aggregation, the substantial intramolecular vibrations are restricted to block nonradiative decay pathway and open the radiative decay pathway. We integrated the RIR with the restriction of intramolecular vibration as the restriction of intramolecular motions (RIM), which will be of great importance for the extending the AIE scope.⁶

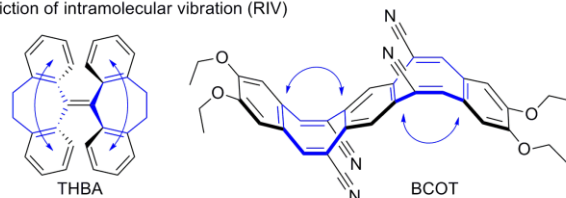
Accordingly, 9,10-bis(diphenylmethylene)-9,10-dihydroanthracene (BDPM-DHA), 5,12-bis(diphenylmethylene)-5,12-dihydrotetracene (BDPM-DHT) and 6,13-bis(diphenylmethylene)-6,13-dihydropentacene (BDPM-DHP)

are designed which contain multiple phenyl groups as rotation parts and dihydroacenes as vibration parts (Fig. 1). All of the three molecules are AIE active, which is in support of our RIM mechanism hypothesis. Furthermore, unprecedented photo-

Restriction of intramolecular rotation (RIR)



Restriction of intramolecular vibration (RIV)



Restriction of intramolecular motion (RIM)

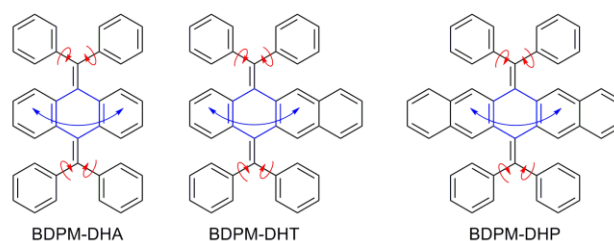


Fig. 1 AIE mechanism hypothesis (red arrow: rotation; blue arrow: vibration) and structures of bis(diphenylmethylene)-dihydroacenes.

chromic effect was found on BDPM-DHT crystals. The colorless BDPM-DHT crystals turned red and their blue emission disappeared upon UV irradiation, which can be gradually recovered via room light treatment.

Photochromic materials have been attracting increasing interest for their great importance in fundamental research and practical applications.⁷ A large number of photochromic systems, including azobenzene,⁸ spiropyran,⁹ diarylethene,¹⁰ etc., have been reported and exhibited good performances in photochemical, biological and nanotechnological applications. However, these systems always have heteroatoms (e.g., N, S, and O), resulting in complicated synthesis, high cost and therefore limited practical applications. Few photochromic systems in the literature are built up on pure hydrocarbon compounds due to their thermo instability. Exploring novel photochromic systems and understanding their working mechanism are drawing continuous attention.¹¹ Particularly, the development of facily synthesized novel photochromic system is highly challenging and demanded.¹² Reported here is a novel aggregation-promoted photochromic system based on pure polycyclic hydrocarbon compound. This system is facily synthesized and exhibits good thermal stability as well as fast photo-response.

Results and discussion

Synthesis, Crystal and Aggregation-Induced Emission

From commercial available acenequinones, BDPM-DHA, BDPM-DHT and BDPM-DHP were synthesized according to the literature method with modifications.¹³ Following typical Corey-Fuchs and Suzuki-Miyaura reactions, grams of final products were obtained in high yield, which were purified by chromatography and recrystallization from chloroform-hexane solution (Scheme S1). Although the syntheses of BDPM-DHA and BDPM-DHP have been reported in earlier literatures,^{13, 14} their AIE properties and crystal structures were further investigated here for the first time.

The photophysical properties of BDPM-DHA and BDPM-DHP were investigated both in their solutions and aggregate states. It was verified that the compounds behave as typical AIE compounds, no emission in their dilute THF solutions and a fluorescence emission at 455 nm and 530 nm, respectively, in their aggregate states (Fig. S4 and S5). Because BDPM-DHP possesses morphology-dependent luminescence property,¹⁵ its emission peak red shifts with increasing water fraction. The solid quantum yields of BDPM-DHA and BDPM-DHP are 15% and 4%, respectively (excited at 325 nm). The AIE properties of BDPM-DHA and BDPM-DHP should originate from the effective RIM process. The excited states in solution decay through nonradiative pathway because of intramolecular motions such as phenyl group rotation and acene backbone vibration. Upon aggregation, these intramolecular motions are restricted. The radiative decay pathway turns on.

Single crystals of BDPM-DHA, BDPM-DHT and BDPM-DHP suitable for X-ray crystallography were grown by slowly diffusing *n*-hexane to CHCl_3 solutions.¹⁶ Shown in Fig. 2 is the crystal structures of BDPM-DHT (grown by slowly evaporation of THF solution). As highlighted in Fig. 2A, the C–C bonds shown in red, green and blue have bond lengths close to typical C–C double bond, single bond and benzene double bond, respectively. These bond lengths indicate that the diphenylmethyl groups have weak conjugation with the tetracene backbone in agreement with its highly contorted structure. Viewed from the side, BDPM-DHT molecule bends

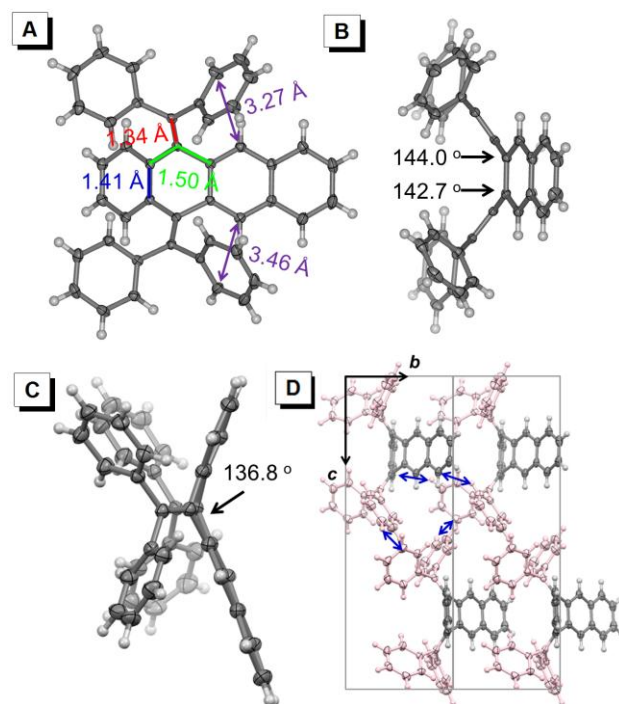


Fig. 2 (A) Top view and (B)–(C) side view of BDPM-DHT with carbon atom positions shown as 50% probability ellipsoids; (D) molecular packing of BDPM-DHT (solvent free) as viewed along the *a* axis of the unit cell with diphenylmethylene group shown in pink. (Carbon and hydrogen atoms are shown in gray and white, respectively.)

by large dihedral angles for both diphenylmethylene groups (Fig. 2B) and tetracene backbone (Fig. 2C). This nonplanar structure can be attributed to the steric repulsion among them. BDPM-DHA and BDPM-DHP in the crystals adopt similar distorted structures as summarized in the Supporting Information (Fig. S1 and S2). Shown in Fig. 2D is the molecular packing of BDPM-DHT, which is built up through weak C–H...C (blue arrow) interactions. As a result, the BDPM-DHT molecules are locked and separated in the crystal. BDPM-DHT crystals become emissive because nonradiative decay pathways such as intramolecular rotation, vibration and π – π interaction were blocked in the crystals.

Aggregation-Promoted Photochromism

As shown in Fig. 3A, colorless needle-shaped crystals of BDPM-DHT exhibit blue emission under UV lamp irradiation (365nm) in accordance with their AIE characteristic. It is unexpectedly found that the colorless crystals became red when the UV lamp was removed, even in a very short irradiation time (~1 second). Meanwhile, the blue emission significantly faded. When placed under room light, the red crystals were gradually returned to colorless accompanied with blue emission recovery. Therefore, BDPM-DHT crystal shows a typical photochromic effect. Meanwhile, the photochromic reaction itself could be considered as the quenching process of the fluorescence. As shown in Fig. S8, the intensity of BDPM-DHA and BDPM-DHP film remained unchanged, indicating they do not show such photochromic effect.

To further investigate color change of the red crystals, they are treated under different conditions. When placed in darkness at room temperature for 2 days, the red crystals remained unchanged, indicating that they are thermally irreversible which is indispensable to the application as optical memories and switches for a photochromic system. When placed at elevated temperature about 60 °C before the crystal collapse (Fig. S9), the red crystals can survive for several hours in darkness. X-ray crystallographic analysis on the red crystals was also performed under dark with continuous UV irradiation (Fig. S10), and the results revealed that they are identical to the colorless ones, suggesting the photochromic reaction occurred in a very small. After cracking the red crystals, the colorless inner part told us that the photochromism occurred only on the crystal surface. Further treating the cracked crystal by UV light, the colorless inner part turned red as origin crystal did, verifying that the photochromism was not induced by impurities on crystal surface. Prolonging the UV irradiation time to 60 minutes, the inner part keeps unreacted, which may be attributed to the UV absorption of red crystal surface.

The UV response of BDPM-DHT in solution state was then tested in 10^{-5} M THF and CHCl_3 solutions monitored by UV-vis absorption. However, no detectable change was observed upon UV irradiation for 5–10 minutes (Fig. S6). Just like the AIE, the aggregation plays an important role in the photochromic process. In the solution, the excited molecules can easily nonradiatively decay through intramolecular motions and solvent molecules collision. Upon aggregation, these pathways were restricted and the blue emission followed by photochromic reaction was facilitated. As a result, it is an aggregation-promoted photochromism system. To exclude the solvate effect of CHCl_3 , solvent-free crystals were successfully obtained and investigated for comparison. As expected, they show similar photochromic behavior under UV and room light irradiation with color change between colorless and yellow. The slight difference in color change is due to the even small amount surface reaction.

Photochromic processes of BDPM-DHT crystals were then investigated by UV-vis reflectance spectroscopy. Before UV irradiation, the colorless crystal exhibits a maximum absorption at 370 nm, which suggests the weak conjugation in the molecules. However, upon irradiation at 365 nm, a strong absorption band peaked at 498 nm emerges and increases with the progress of photo-irradiation (Fig. 3B). The absorbance reaches half-peak width within 5 seconds and saturates after 60 seconds. Additionally, the progress of room light response was also recorded using the same method (Fig. S7). The increase and the decrease of the reflectance at 498 nm as a function of time were plotted and used to monitor the photo response processes. As shown in Fig. 3C, the crystals responded rapidly in the first 10 seconds and almost finished in 60 seconds towards UV and visible light. As shown in Fig. 3D, BDPM-DHT crystals were repeatedly switched between the red and colorless state for 10 times, and the reflectance at 498 nm stayed almost constant without any apparent degradation, indicating their good fatigue resistance.

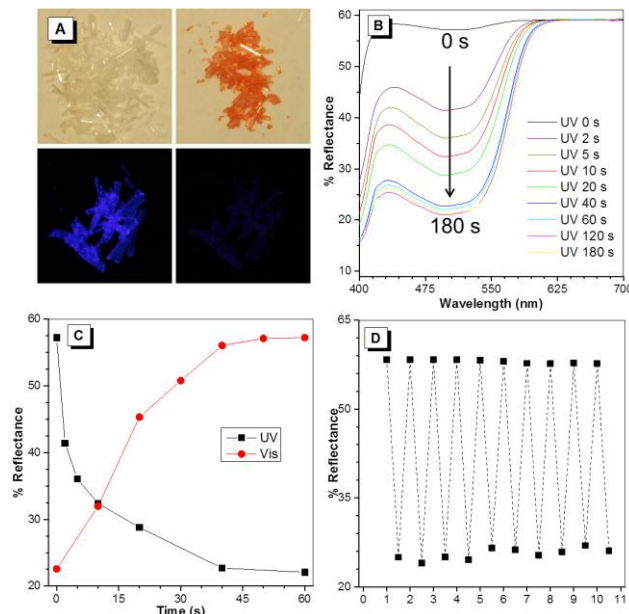


Fig. 3 (A) Up: room light images of BDPM-DHT crystals before (left) and after (right) UV irradiation; Down: UV light images of BDPM-DHT crystals before (left) and after (right) UV irradiation. (B) Changes in the UV-vis reflectance spectra of BDPM-DHT crystal upon irradiation at $\lambda = 365$ nm. (C) The plot of the reflectance change at $\lambda = 498$ nm as a function of UV irradiation and visible light exposure time. (D) Fatigue resistance of crystal BDPM-DHT upon irradiation with 365 nm (1 minute) and standing in room light (1 minute) alternatively. (The reflectance was measured at 498 nm.)

Photochromic Mechanism

For the presence of two fixed *cis*-stilbene motifs and short distance between the phenyl ring and the tetracene backbone (Fig. 2A), mechanism for the color change of BDPM-DHT crystal upon UV irradiation was proposed as depicted in Fig. 4. Here, the photochromic effect of BDPM-DHT is ascribed to photo-induced ring closing from BDPM-DHT to DPBNP-H, which has a larger π conjugation as highlighted in bold-red line. DFT calculation, further crystal structures analysis and photo oxidation reactions were applied to verify the photochromism hypothesis and investigate the DPBNP-H intermediate.

From BDPM-DHT to DPBNP-H, three benzene rings are broken. However, after DFT calculation, we found the energy difference between BDPM-DHT and DPBNP-H is merely about 149 kJ/mol, which is close to the resonance energy of only one benzene ring. The newly formed π -conjugation was thought to make a big contribution to stabilize the intermediate DPBNP-H. The possibility in photocyclization on the benzene-ring side rather than that on the naphthalene-ring side was partially excluded because of even larger energy difference between BDPM-DHT and DPBNP-H' of 172.6 kJ/mol (Fig. S13).

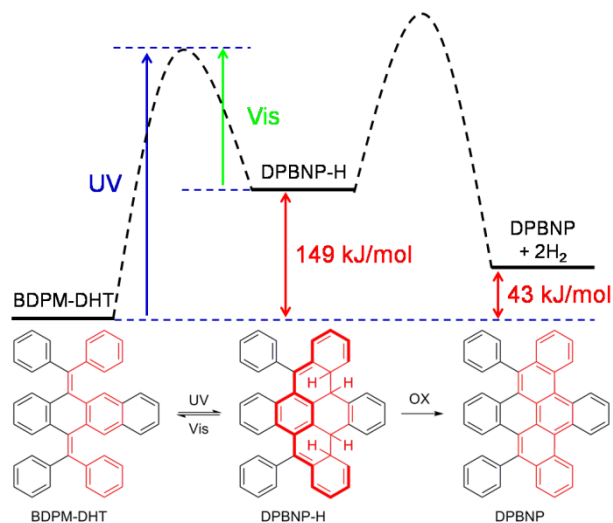


Fig. 4 Proposed mechanisms of the photochromic process and calculated reaction coordinate diagram.

Meanwhile, the same calculations were performed on BDPM-DHA and BDPM-DHP systems. The energy difference increases to 158 kJ/mol for BDPM-DHA and 164 kJ/mol for BDPM-DHP, respectively. Although the calculation results are in agreement with their no photochromic behavior (see Figure S11), energy differences among three systems are relatively small. We further study their molecular and crystal structural differences. Among the three systems, BDPM-DHT has the highest similarity between backbone of BDPM-DHT and that of DPBPNP-H. For BDPM-DHT, the aromatic parts of tetracene backbone keep almost no change before and after the cyclization, regarding as one naphthalene ring and one benzene ring. However, for BDPM-DHA, the aromatic parts of anthracene backbone change from two benzene rings to one naphthalene ring. For BDPM-DHP, the aromatic parts of pentacene backbone change from two naphthalene rings to one anthracene ring and one benzene ring. According to the Clar's rule, such changes are disfavored in energy. As summarized in Table S2, although all of the distances between the possible photoactive carbon atoms are less than 4.2 Å required for solid photocyclization,¹⁷ BDPM-DHT (solvent-free and CHCl₃) molecules in their single crystals have the shortest distance pairs than BDPM-DHA and BDPM-DHP, indicating the highest possibility of electronic cyclization reaction and being exhibited by their UV irradiation responses.

In the presence of air, the dihydrophenanthrene can be oxidized to phenanthrene irreversibly. To further verify the mechanism, we also tried to get oxidation product DPBPNP from the intermediate DPBPNP-H as the indirect proof. Firstly, we extended the UV irradiation time to 2 days in air. The BDPM-DHT crystal surface irreversibly turned yellow and a peak related to the DPBPNP appeared in high-resolution mass spectrum (Fig. S14). In contrast, the BDPM-DHT crystal successfully recovered to colorless after irradiated in N₂ atmosphere for 24 hours without oxidation. Secondly, we used Katz-modified Mallory photocyclization method to treat BDPM-DHT.¹⁸ DPBPNP was obtained in a high yield. To our surprise, the reaction was completed in 20 minutes, which was much faster than that of BDPM-DHA and BDPM-DHP.¹⁹ The photochromic effect of BDPM-DHT should help the formation of dihydro intermediate and accelerate the reaction. The DPBPNP structure tells us that the photocyclization reaction

occurred at naphthalene-ring part. It was worth noting that the DPBPNP is an aggregation-induced quenching molecule, which is opposite to its precursor BDPM-DHT (AIE). The partial lock of phenyl rings and large π -plane formation should account for this property.

Though control irradiation and photocyclization product analysis, the dihydro intermediate was believed as the most possible photochromic product via 6- π electronic cyclization reaction. The theoretical calculations also prove the proposed mechanism. Due to small amount and the fast response towards room light, continuous efforts were expressed to find DPBPNP-H but failed. It is well known that *cis*-stilbene can undergo a photo-cyclization reaction to yield dihydro-phenanthrene.²⁰ However, dihydrophenanthrene is highly unstable and returns to stilbene very quickly even in the darkness,²¹ which sets an obstacle to characterize the dihydro-intermediate (e.g., DPBPNP-H in our system). Therefore, phenyl rings of stilbene are usually replaced by hetero aryl rings such as thiophene, furan and pyrrole to prolong the lifetimes of the dihydro intermediates, because hetero aryl rings have smaller aromaticity.²¹ Therefore, 5, 12-bis(dithiophenylmethylene)-5, 12-dihydrotriacene (BDTM-DHT) was chosen for further mechanism verification. The backbone is the same as the BDPM-DHT, but four thiophenyl groups were used to replace the four phenyl groups. The amount of photochromic reaction in BDTM-DHT was enhanced due to smaller aromaticity of thiophene ring. The photocyclization mechanism would be directly proved by the existence of cyclized-BDTM-DHT (*c*-BDTM-DHT). As predicted (Fig. S15), upon photocyclization signals at ~4 ppm relating to alkyl protons and signal at ~6.5 ppm relating to vinylic protons appear. As shown in Fig. S16-17, after UV irradiation, signals at 4.4 ppm, 4.8 ppm, and 6.4 ppm were observed in both CDCl₃ and CD₂Cl₂ solution. Although they are poorly resolved, these new-formed signals still indicate the existence of *c*-BDTM-DHT. The difference from the predicted spectra may arise from chirality and asymmetry of *c*-BDTM-DHT structure or one-side photo-cyclization product. The weak intensity of signals suggests low quantum yield of our photochromic system.

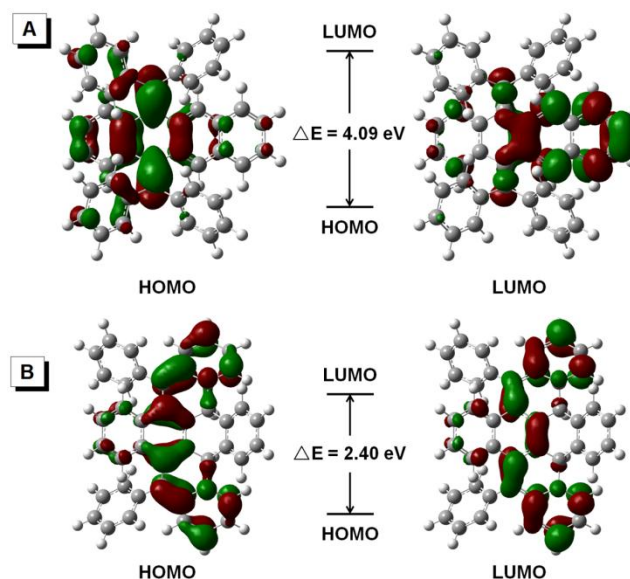


Fig. 5 Molecular orbital amplitude plots (isovalue=0.03) of HOMO and LUMO energy levels of BDPM-DHT (A, open form) and DPBPNP-H (B, closed form).

As shown in Fig. 5, the HOMO and LUMO energy levels of BDPM-DHT are calculated and found localized at dimethylene-cyclohexadiene part and the naphthalene part, respectively, proving its weak intramolecular conjugation and distorted structures. For DPBNP-H, both HOMO and LUMO are delocalized throughout the newly formed π -electrons. Meanwhile, the energy gap between the HOMO and LUMO is dramatically decreased from 4.09 eV to 2.40 eV, which are in good agreement with its optical energy gap and the color change from colorless to red.

Conclusions

In summary, this study puts forth a new photochromic system based on an AIE luminogen, which is conducted by a pure polycyclic hydrocarbon compound without any heteroatoms. Grams of BDPM-DHT were successfully synthesized through simple reactions. Particularly, fast responsive, photo-reversible and thermo-irreversible photochromic properties were realized in the solid state, which are crucial for practical application. Photocyclization reaction was proposed as the mechanism for the photochromic process, whose energy barrier is partially counterbalanced by newly formed π -conjugation and the tetracene backbone. Similar to AIE, the only solid-state photochromic response makes BDPM-DHT the first aggregation-promoted photochromic system, which is facilitated by RIM and functions as a novel photochromic system.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Details of the synthesis and characterization, the crystallographic information files (CIF), ¹H NMR, ¹³C NMR, and HRMS spectra, UV and PL spectra and details of the DFT calculations are in the supporting information. See DOI: 10.1039/b000000x/
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