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Pressure-Induced Blue-Shifted and Enhanced Emission: A Cooperative Effect between Aggregation-Induced Emission and Energy-Transfer Suppression

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Supporting Information Placeholder

ABSTRACT: Most organic piezochromic materials exhibit red-shifted and quenched emission as pressure increases. However, an abnormal phenomenon of pressure-induced blue-shifted and enhanced emission is observed in a 9-(3-(1,2,2-triphenylvinyl)phenyl)anthracene crystal, which is based on discrete π-π anthracene (AN) dimer stacking with tetraphenyl ethylene (TPE) as a spacer. A blue-shifted emission appears and strengthens when pressure is more than 1.23 GPa, and it reaches the maximum when pressure is 4.28 GPa. This phenomenon is ascribed to the cooperative effect between the aggregation-induced emission of TPE units and energy-transfer suppression from TPE to an AN excimer. This work reports a new concept in the piezochromic field and provides a novel strategy to achieve luminescence from a high-lying excited state.

Piezochromic luminescent materials exhibit remarkable emission color changes in response to external mechanical stimuli (e.g., grinding, pressing, and stretching), and such materials have been widely explored because of their potential for applications in optical data storage, pressure sensors, and optoelectronic devices.[1-20] Their mechanism mainly involves the changes in chemical structures (i.e., breaking and reforming chemical bonds),[21-23] phase transition (e.g., crystal-to-crystal[24,25] and crystal-to-amorphous[26-29]), conformational transformation,[30-32] and excited-state transformation (e.g., locally excited state to charge-transfer state,[33,34] triplet state to singlet state[35,36], and monomer state to excimer/exciplex state).[37,38] However, more universal and innovative strategies are required to design novel materials for the specific applications of piezochromic luminescence because current mechanisms usually cannot be integrated from one system to another.

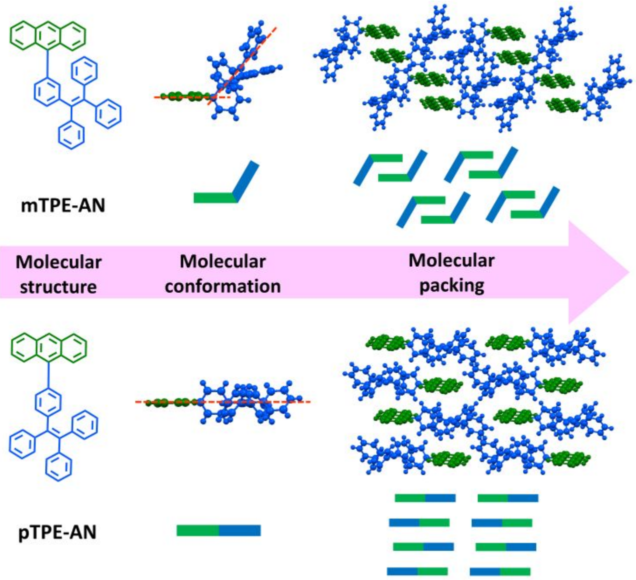

Figure 1. Molecular design for discrete AN dimer formation. Molecular conformation and crystal packing were obtained through single-crystal XRD experiment.

Among mechanical forces, isotropic hydrostatic pressure from a diamond anvil cell (DAC) is a useful tool to investigate structure–property relationships.[39] Most luminescent materials show a gradual red-shifted and quenched emission as pressure increases as a result of the formation of a low-energy emission species and a nonradiative "dark" state (e.g., narrow-bandgap excimer).[40-45] Although few cases have been reported with pressure-induced blue-shifted emission,[46-49] simultaneous pressure-induced blue-shifted and enhanced emission has not been reported in π-conjugated organic materials.[6-20]

Tetraphenyl ethylene (TPE), a typical aggregation-induced emission (AIE) luminogen,[50,51] exhibits a pressure-induced emission enhancement[44,45] because of the inhibition of intramolecular motions under pressure. By contrast, the enhanced π-π interaction in an anthracene (AN) dimer during compression usually leads to the gradual redshift and quenching of excimer fluorescence.[52-54] In our work, we combined TPE and AN into one molecule to design a new compound, namely, 9-(3-(1,2,2-triphenylvinyl)phenyl)anthracene (mTPE-AN), which demonstrated a rare piezochromic luminescent behavior upon the application of pressure in crystals: pressure-induced emission blue-shift and enhancement by the cooperation between AIE and suppressed energy transfer (ET) from TPE to an AN excimer.

A design strategy was proposed on the basis of molecular structure, conformation, and packing. The *meta*-linkage of mTPE-AN between an AN core and a one-sided TPE substituent was designed for the possible formation of the target dimer (**Figure 1 and S7**). The TPE substituent is asymmetrically oriented along one side of the AN plane in molecular conformation, which favors AN dimer formation with antiparallel π-π stacking.[55-58] For comparison, a counterpart of 9-(4-(1,2,2-triphenylvinyl)phenyl)anthracene (pTPE-AN)[59] was designed with a *para*-linkage between the AN core and the one-sided TPE substituent. The TPE substituent in the molecular conformation of pTPE-AN was divided equally by the AN plane, resulting in a complete deviation of π-π AN dimer stacking in crystals. mTPE-AN was synthesized via a boride reaction followed by two-step Suzuki coupling reactions, and pTPE-AN was produced via a one-step Suzuki coupling reaction (Supporting Information). Single crystals of mTPE-AN and pTPE-AN were cultivated through slow solvent evaporation from their dichloromethane/methanol solutions. mTPE-AN crystals showed a largely red-shifted, structureless, and broadened emission spectrum (λ_{max} = 518 nm) and prolonged lifetime (τ = 191.70 ns; **Figure S8-10**) compared with those from single-molecule emission. These findings agreed with the characteristic of an AN excimer.[52-54,60-62] mTPE-AN crystals exhibited a high photoluminescence quantum yield (PLQY) of 82.20% as a result of the excimer-induced emission enhancement mechanism (**Figure S11** in Supporting Information).[8,55-58] By comparison, pTPE-AN crystals displayed a monomer-like blue emission with λ_{max} = 432 nm, short lifetime of τ = 8.05 ns, and PLQY of 68.24%.

A single-crystal X-ray diffraction (XRD) experiment under ambient conditions was performed to confirm the feasibility of the molecular design strategy as mentioned above (**Figure 1**). In mTPE-AN crystals, TPE units acted as spacers to isolate the π-π AN dimer from one another. No interaction existed between one dimer and adjacent dimers, that is, isolated and discrete π-π dimer stacking in mTPE-AN crystals.[55-58,61,62] The interplanar π-π distance between two AN units in a dimer is 3.527 Å, and the overlapped area is approximately 32%, indicating a strong π-π interaction (**Figure S12**).[63] According to density functional theory calculations, the natural transition orbitals of the dimer indicate that the high PLQY of mTPE-AN crystals can be ascribed to the hybridized local and charge-transfer state (**Figures S13–S16**, see Supporting Information for details).[64-66] By contrast, pTPE-AN crystals showed the nondimer stacking of AN (**Figures S17** and **S18**).

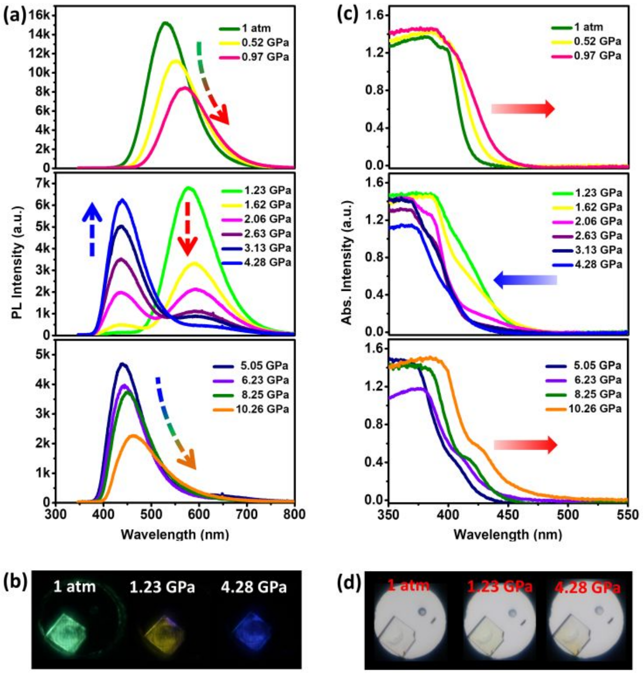

Figure 2. (a) Emission spectra, (b) fluorescent images, (c) absorption spectra and (d) visible images of mTPE-AN crystals under pressure from 1 atm to 10.26 GPa.

Here, shearing force was applied to a crystalline sample of mTPE-AN by grinding for 60 min, but no change was observed in the emission and XRD pattern (**Figure S19**). This result indicated that the crystalline mTPE-AN sample was stable enough and thus remained undisturbed by grinding.[8,57] As an alternative, the isotropic hydrostatic pressure was directly exerted via a DAC on mTPE-AN crystal (for experimental details, see Supporting Information), and obvious three-step variations were observed (**Figures 2, S20,** and **S21**). As pressure increased from 1 atm to 1.23 GPa, mTPE-AN crystal showed the gradual red-shifted emission of the AN excimer from green to yellow (herein called low-energy emission band for clarity) and the decreased intensity, together with the slightly red-shifted absorption onsets. Once pressure increased above 1.23 GPa, the emission band of approximately 438 nm (called high-energy emission band) suddenly appeared and then gradually increased. Moreover, the high-energy emission band reached its maximum intensity at 4.28 GPa; the intensity of low-energy emission band kept decreasing, giving rise to pure blue emission. The absorption onset also kept the blue-shifted trend until 4.28 GPa. With further compression of over 4.28 GPa, high- and low-energy emission bands demonstrated a redshift and an intensity decline. The absorption onset was unceasingly red-shifted. In compression, the blue-shift and enhancement of the emission spectra resulted in a discontinuous change in emission color from green and yellow to blue, which was opposite of the majority of observations in the piezochromic luminescent field. However, after a high pressure of up to 12.48 GPa was exerted on pTPE-AN crystal (**Figure S22**), continuous red-shifted and quenched emission was observed from 432 nm to 532 nm. This observation was different from that of mTPE-AN crystal under pressure. Although blue-shifted emission has been reported for carbon dots under hydrostatic pressure,[47-49] carbon dots have no clear structural information at a molecular level. Consequently, studying the structure–property relationship is difficult. In this experiment, mTPE-AN crystal had a definite molecular structure and packing arrangement, which was highly desired to establish a structure–property relationship.

Two possibilities were responsible for the emergence of the high-energy emission band of mTPE-AN crystal under pressure: phase transition from dimer to monomer and chemical reaction. On the one hand, the high-pressure angle-dispersive XRD experiment showed that all representative diffraction peaks during compression shifted to high angles. No disappeared peaks as well as no sudden new peaks were observed (**Figure S23**), excluding the occurrence of phase transition. Moreover, all three axes of a unit cell were shortened, and volume was reduced as pressure increased. Thus, dissociating one AN dimer into two AN monomers was impossible because mTPE-AN crystal became much more closely packed throughout compression. Actually, the low-energy emission band from the AN excimer existed throughout compression and just accompanied with a continuous redshift and a decreasing intensity. On the other hand, after the crystalline mTPE-AN powder was irradiated with UV light for 32 h, its ^{1}H NMR spectrum remained the same as the one before irradiation (**Figure S24**), excluding the photodimerization of the AN dimer.[67,68] Moreover, the mass spectrum (MS) of mTPE-AN crystals under 2.00 GPa was identical to the MS of a pristine sample (**Figure S25**). This result indicated no chemical reaction in mTPE-AN crystals.

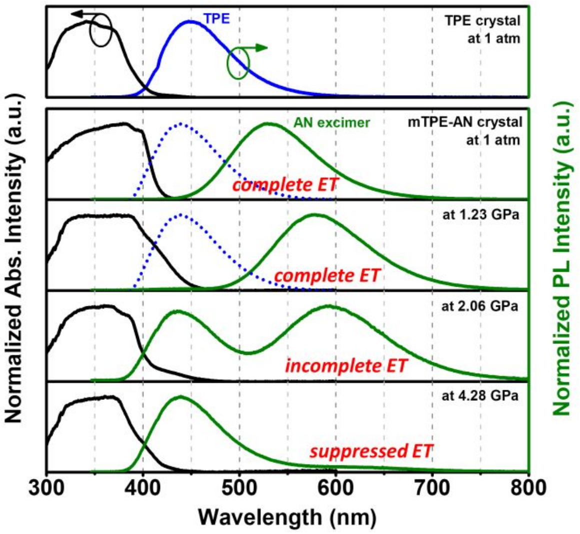

Figure 3. Normalized absorption and emission spectra of TPE crystals at 1 atm and mTPE-AN crystals at 1 atm ~ 4.28 GPa. Dotted curve depicts the quenched emission spectrum of TPE to estimate the spectral overlap for ET process from TPE to AN dimer.

Pressure-dependent structural simulation in mTPE-AN crystal showed the decreasing π-π distance of the AN dimer and the TPE dimer, corresponding to the enhancement of intermolecular interactions with increasing pressure through Hirshfeld surface analysis (**Figures S26-S29, Table S2, and Table S3**). As pressure further increased, more interactions were combined, and intramolecular vibrations and rotations of the TPE units could be effectively restricted for the decreased nonradiation, resulting in the AIE behavior of TPE. In **Figure 3**, almost the same emission and absorption bands were observed between TPE crystal at 1 atm and mTPE-AN crystal at 4.28 GPa, indicating that the blue-shifted emission band in mTPE-AN crystal under pressure might originate from the TPE units.

The time-resolved spectrum and the excitation wavelength dependence were obtained at room and low temperature to understand the mechanism of pressure-induced emission blue-shift and enhancement in mTPE-AN crystals. To some extent, the effect of low temperature on the decrease in π-π distance was the same as that of high pressure (**Figure S30**).[42] At room temperature (RT), mTPE-AN crystals showed single-exponential fluorescence decay from the time-resolved spectrum (**Figure S31a**), corresponding to a single pure excited state of the AN excimer. Moreover, the excitation-independent emission wavelength at RT suggested a rapid internal conversion (IC) process, i.e., a complete ET from TPE to an AN excimer (**Figure S31b**). However, mTPE-AN crystals exhibited two-exponential fluorescence decay at 80 K (**Figure S31c**). This result indicated a suppressed ET from TPE (donor) to the AN excimer (acceptor).[69] The excitation-dependent emission spectra at 80 K revealed two emission bands from TPE and the AN excimer and confirmed the suppressed ET from TPE to the AN excimer (**Figure S31d**).

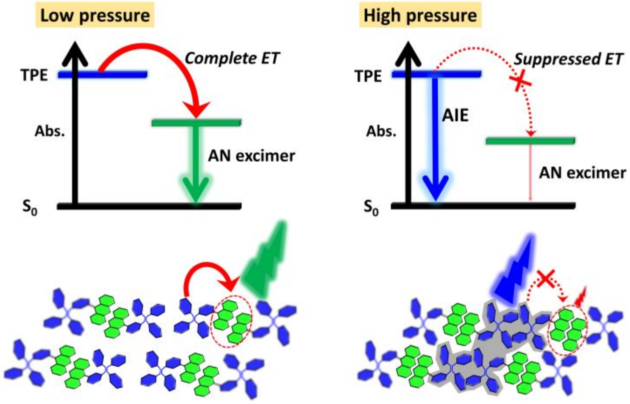

Figure 4. Schematic diagram of pressure-induced emission blue-shift and enhancement in mTPE-AN crystals.

Pressure-induced emission blue-shift and enhancement during mTPE-AN crystal compression can be explained as follows. From 1 atm to 1.23 GPa, the complete ET from TPE to the AN excimer produces the only emission band of the AN excimer because of the gradually increasing spectral overlap between TPE emission and AN dimer absorption (**Figure 3**). When pressure exceeds 1.23 GPa, the absorption of the AN dimer weakens because of the forbidden transition (**Figure S32**) and the disappearance of AN monomer absorption, while the emission spectra of TPE remain almost unchanged. Thus, the continuously reducing overlap between TPE emission and AN dimer absorption leads to the suppressed ET,[70] which is responsible for the emerging high-energy emission band of TPE. TPE units aggregate into a tighter packing as pressure increases, thereby triggering the AIE mechanism of the enhancement of the high-energy emission band (**Figure 4**). Once pressure exceeds 4.28 GPa, the high-energy emission band is gradually quenched probably because a stronger π-π interaction between TPE units leads to the formation of the energy-trapping "dark" state. For the redshift and quenching of the low-energy emission band with increasing pressure, the energy gap dramatically narrows between the potential energy curves of the excimer at an excited state and the dimer at a ground state because of the decreased π-π distance. Consequently, the nonradiative IC rate is aggravated according to the energy gap law. When the released pressure is 1 atm, the emission band of the AN excimer becomes reversible, but a small spectral residue of the high-energy emission band is observed (**Figures S33** and **S34**). This spectral residue might result from the hysteresis effect that TPE units experience difficulty in promptly restoring their geometries to the original state because of the large structural deformation at pressures above 1.23 GPa.

In conclusion, mTPE-AN, a new piezochromic compound, was designed and synthesized, and it consisted of two functional moieties with a meta-linkage: an AIE-featured TPE and an excimer-forming AN. The discrete π-π dimer stacking of the AN was obtained in crystal with TPE unit as a spacer. An abnormal phenomenon of pressure-induced emission blue-shift and enhancement of mTPE-AN crystal was discovered. This phenomenon was an extremely rare case in the field of piezochromic luminescence. Theoretical and experimental investigations demonstrated that the blue-shifted emission band originates from the TPE units in the mTPE-AN crystal. The suppressed ET from TPE to AN dimer induces the appearance of a blue-shifted band from 1.23 GPa to 4.28 GPa, and the AIE mechanism of TPE units contributes to the enhancement of the blue-shifted emission band, which is cooperatively responsible for pressure-induced emission blue-shift and enhancement. This work reports a novel principle for a new class of blue-shifted and enhanced piezochromic luminescent materials by using the combination between ET suppression and AIE activation. This study also presents an ideal model to improve the understanding of high-lying excited-state emission in fundamental photophysics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Characterization methods, synthetic details, ^{1}H NMR spectra, ^{13}C NMR spectra, MS, UV-vis spectra, AIE characteristic, powder XRD, crystal packing structure, NTOs, pressure-dependent emission spectra of pTPE-AN crystal, theoretical simulation of mTPE-AN geometry under pressure, Hirshfeld surface analysis, temperature-dependent emission spectra of mTPE-AN crystal, spectral reversibility

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The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡These authors contributed equally.

Notes

The authors declare no competing financial interests.

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