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Tuning the photophysical properties of symmetric squarylium dyes: investigation on the halogen modulation effects

Weiben Chen,[a]† Simeng Zhang,[a]† Gaole Dai,[b] Ying Chen,[a] Miao Li,[a] Xiaoyu Zhao,[a] Yulan Chen*[a] and Long Chen*[a]

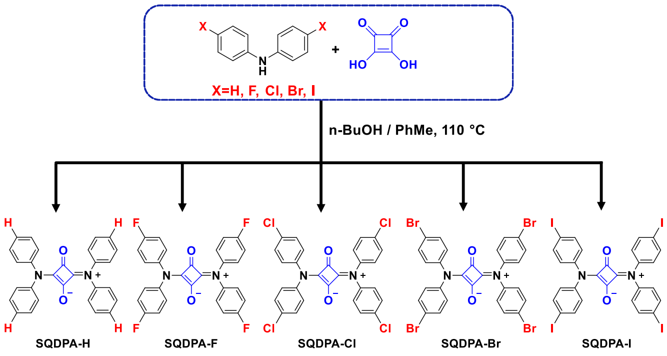
Abstract: A series of symmetric squarylium dyes (SQDPA-X) with different halogen (X = F, Cl, Br, I) substituents have been developed. The photophysical properties could be facilely tuned by the halogen modulation effects. The strategy of incorporating different halogen substitutions into AIE active luminogens enables a facile approach for exploring new intriguing organic fluorescent dyes.

Organic fluorescent dyes have gained increasing interest on account of their substantial applications in organic light-emitting diodes,[1] bioimaging,[2] dye-sensitized solar cells,[3] nonlinear optical materials,[4] etc. It is well known that most of the luminophores usually tolerate a pronounced decreasing of their fluorescence in aggregated states, known as aggregation caused quenching (ACQ) effect.[5] In contrast, some particular chromophores are emissive in the aggregated states. This unconventional photophysical phenomenon is coined as aggregation-induced emission (AIE) by Tang and co-workers.[6] The comprehensive mechanism for the unique phenomenon was clarified to be the restriction of intramolecular rotations (RIR).[7] Most of AIE active luminogens (AIEgens) possess propeller-like or flexible moieties such as diphenylamine,[8] triarylamine,[9] tetraphenylethylene[10] etc. Currently, except for the above-mentioned applications, AIEgens based stimuli-responsive fluorochromic materials[11] have also been developed.[12]

Fluorochromic materials with reversible colour change triggered by external stimuli are an important category of smart materials.[13] Up to now, several types of fluorochromic materials have been developed such as photochromic,[14] electrochromic,[15] thermochromic,[16] mechanochromic,[17] solvatochromic[18] and vapochromic[19] materials. Among them, mechanochromic materials with reversible fluorescence change by mechanical stress have made rapid progress.[20]

Squaric acid is an electron deficient motif with a four membered ring, which can react with electron donating groups to form a donor–acceptor–donor (D–A–D) system.[21] Theoretical simulation suggests that the ground state and excited singlet state of squarylium dyes (SQDs) exhibit distinctive intramolecular charge transfer (ICT) behavior.[22] To the best of our knowledge, SQDs with both AIE and fluorochromic properties have not yet been explored. In this context, we herein reported a new series of symmetric SQDs derivatives (i.e. SQDPA-F, SQDPA-Cl, SQDPA-Br, SQDPA-I) with typical AIE, mechanochromic and vapochromic properties by different halogen (X= F, Cl, Br, I) modulation effects (Scheme 1). These SQDs were ambiguously characterized by UV-vis absorption spectroscopy, powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), single crystal diffraction analysis and theoretical modelling.

The SQDs were facilely synthesized by the condensation of squaric acid with diphenylamine derivatives in toluene and n-butyl alcohol at 110 °C (Scheme 1).[23] The photophysical properties of all SQDs was first investigated by UV-vis spectra performed in DMF solutions. As shown in Figure 1, the intense absorption peaks at 406 to 425 nm can be correlated to the HOMO-LUMO transitions (385.18 nm to 396.05 nm, oscillator strength f = 0.6071 to 0.7601) based on the time dependent density functional theory (TD DFT) calculations (CAM-B3LYP/6-31G**) (Table S4, Figure S32). The red shift sequence of simulated absorption maxima peaks also match with the experimental spectra, i.e. SQDPA-F, SQDPA-H, SQDPA-Cl, SQDPA-Br, SQDPA-I. Obvious red-shifts in absorption and emission maximum of these SQDs were observed as the halogen atomic number increased.[24] To further compare the electronic structures of these SQDs, DFT calculations at the B3LYP/6-31G** level were carried out.[25] The HOMOs for all SQDs are π orbitals mainly localized on the central cyclobutene cores, while π* orbitals of the LUMO are primarily distributed over the peripheral groups (Figure S31 and Table S3). The observed optical bandgaps (E_{obg}) were 2.29 eV, 2.27 eV, 2.24 eV, 2.23 eV, 2.20 eV for SQDPA-F, SQDPA-H, SQDPA-Cl, SQDPA-Br, SQDPA-I, respectively, which are in accordance with the calculated energy band gaps (E_g), following the same trend of SQDPA-F (3.334 eV) > SQDPA-H (3.323 eV) > SQDPA-Cl (3.283 eV) > SQDPA-Br (3.278 eV) > SQDPA-I (3.261 eV) (Table S3, Figure S31). These results illustrate that the introduction of halogen atom can modulate the photophysical properties of squarylium dyes.



Scheme 1. Synthesis of symmetric squarylium dyes containing different halogen substituted diphenylamine derivatives

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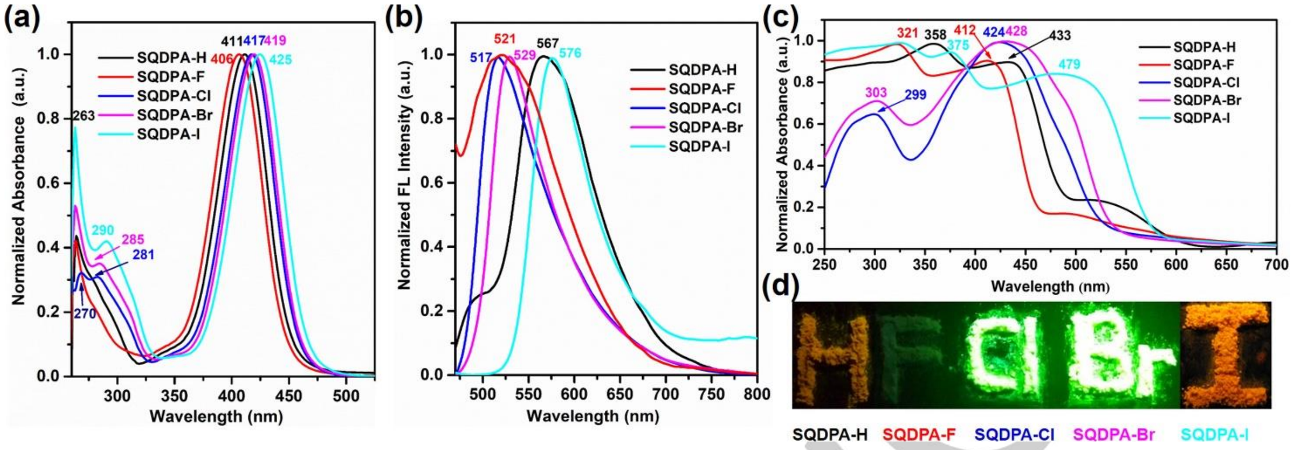

Figure 1. (a) UV-vis absorption spectra of SQDs (1.0×10^{-5} mol/L in DMF); (b) solid-state fluorescence spectra and (c) solid-state absorption spectra of SQDPA-H (black line), SQDPA-F (red line), SQDPA-Cl (blue line), and SQDPA-Br (pink line) SQDPA-I (green line); (d) the fluorescence images of all SQDs

The AIE characteristics of these new luminogens (i.e. SQDPA-F, SQDPA-Cl, SQDPA-Br, SQDPA-I) were elucidated in detail (Figure 2 and Figure S15-S16). All these newly halogen substituted SQDs were nonluminous in DMF or THF solutions but emitted bright green light when proper amount of water was added. The fluorescence significantly enhanced when the water fraction (f_w) exceeded a critical point (f_w = 30%, 20%, and 30% for SQDPA-Cl, SQDPA-Br, SQDPA-I, respectively). The emission further enhanced with adding more water. However, the fluorescence intensity descended when the fraction of water f_w exceeded 60%, 40%, and 70% for SQDPA-Cl, SQDPA-Br, SQDPA-I, respectively. It was demonstrated that large nanoaggregates were formed and precipitated in these cases by the dynamic light scattering analysis (Figure S24-S26).[26]

Luminophores with bright emission in solid state usually exhibit tunable optical properties upon external stimuli, which reminds us to explore the mechanofluorochromism (MFC) behaviour of these SQDs. For example, SQDPA-F displays distinct fluorescence enhancement upon grinding. The fluorescence quantum yield (φ_F) slightly increased from 4.80% to 5.45% (Table S2) and the solid-state fluorescence lifetime also increased from 0.37 ns to 0.55 ns after grinding (Table S5). In contrast, SQDPA-Cl and SQDPA-Br exhibit typical mechanochromic behaviours upon external mechanical stimulation (Figure 3). The emission bands of SQDPA-Cl (Figure 3a) and SQDPA-Br (Figure 3b) were broadened upon grinding. And the fluorescence quantum yields of SQDPA-Cl and SQDPA-Br in the pristine state (49% and 34%, respectively) were higher than those in the ground state (15% and 14%, respectively). The solid-state fluorescence lifetime of SQDPA-Cl and SQDPA-Br also decreased (Table S5). The largest fluorescence red-shift was 56 nm for SQDPA-Cl and 65 nm for SQDPA-Br after grinding. The emission maxima of the ground SQDs was blue-shifted to the original state after fuming with THF vapor and the intensity was enhanced as well. The reversible fluorescence switching has been demonstrated with SQDPA-Cl and SQDPA-Br for at least five cycles without significant changes (Figure S20). Such good fluorescence fatigue resistance is of great significance for application in sensors or security inking.[27]

Powder X-ray diffraction (PXRD) measurements were conducted to unveil the origin of the mechanochromism (Figure S17-S18). For the ground SQDPA-F, SQDPA-Cl and SQDPA-Br samples, most of the diffraction peaks decreased compared with the pristine ones, which demonstrated that the crystalline structures have been substantially demolished to the partial amorphous states. The remained weak diffraction peaks might be ascribed to the insufficient grinding. The diffraction peaks of the ground SQDPA-Cl and SQDPA-Br samples were greatly enhanced after fuming with THF, which confirmed the recovery of an ordered crystalline state. Differential scanning calorimetry measurement was carried out for all SQDs (Figure S28). Only SQDPA-Cl and SQDPA-Br exhibited apparent endothermic peaks at 145 °C and 160°C, respectively, which refered to the phase conversion from metastable amorphous state to the ordered

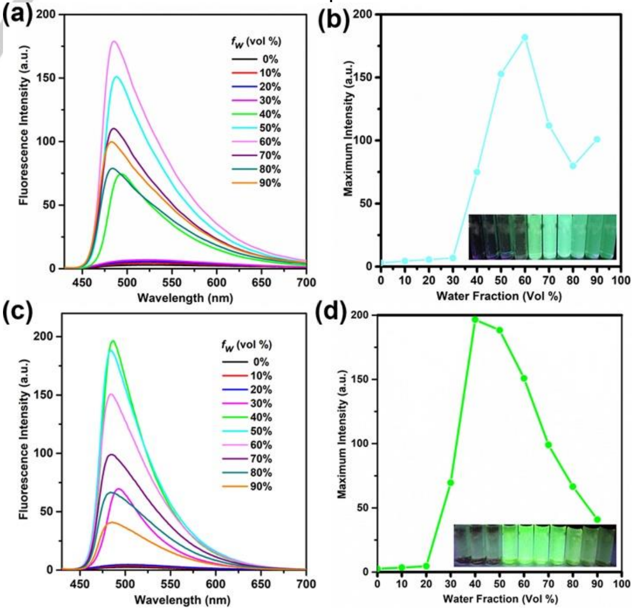

Figure 2. Fluorescence spectra of the dilute solutions of (a) SQDPA-Cl and (c) SQDPA-Br in DMF/H_2O with different f_w; plot of fluorescence intensity maximum of (b) SQDPA-Cl and (d) SQDPA-Br; Inset: fluorescence images of (b) SQDPA-Cl and (d) SQDPA-Br in DMF/H_2O mixtures

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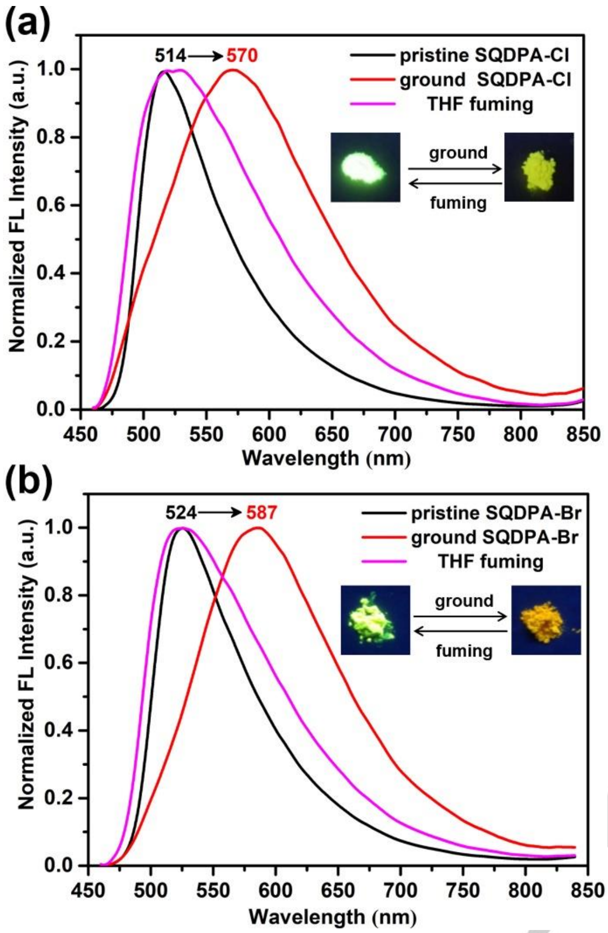

Figure 3. Normalized solid-state fluorescence spectra of (a) SQDPA-Cl and (b) SQDPA-Br before (black line) and after (red line) grinding and upon THF (pink line) fuming. Inset: Photographs of (a) SQDPA-Cl and (b) SQDPA-Br before and after grinding and organic solvent fuming.

microcrystalline state.[28]

The mechanochromism of SQDPA-I was not obvious, but it showed distinctive vapochromic feature toward different organic solvents (Figure 4). The red orange colour of the pristine SQDPA-I changed to bright yellow when fuming with $CHCl_3$, CH_2Cl_2 or THF (good solvents). The emission maximum was blue-shifted from the original 577 nm to 537 nm. Meanwhile, the fluorescence quantum yield of pristine SQDPA-I was dramatically increased to 29.4% upon CH_2Cl_2 fuming (Table S2). The solid-state fluorescence lifetime was also increased from 0.22 ns to 1.44 ns (Table S5). It is interesting that the color of SQDPA-I could be recovered to the initial red orange upon fuming with ethyl acetate (EA, poor solvent). Moreover, this reversible color change could be repeated for at least five cycles upon alternative fuming with $CHCl_3$ and EA vapor (Figure S19b). The PXRD pattern of SQDPA-I slightly exhibited attenuation after grinding. However, the PXRD pattern of SQDPA-I greatly changed when exposed to $CHCl_3$ vapor (Figure S19a). In addition, PXRD patterns of SQDPA-I after $CHCl_3$ fuming (red line) was similar to the simulation SQDPA-I XRD (black line) based on the single crystal data (Figure S23). Meanwhile, the DSC of SQDPA-I after $CHCl_3$ show apparent endothermic peaks at 105 °C, which was due to the crystal state conversion (Figure S29). We further measured the UV-vis absorption spectra of SQDPA-I at different color states (Figure S22b). It revealed that the absorbance maximum was blue-shifted from 478 nm to 423 nm, which was similar to the absorbance maximum in $CHCl_3$ (425 nm) (Figure S22a). The above results indicate that the molecular packing could be loosen when SQDPA-I is fuming with $CHCl_3$, while it could be re-condensed upon fuming with EA. The different photophysical properties should originate from the different packing modes.

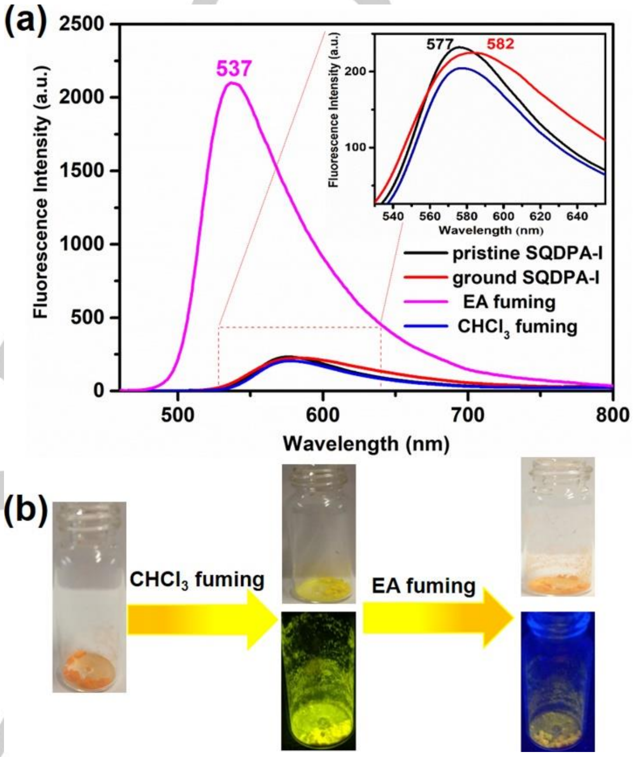

Figure 4. (a) fluorescence spectra of SQDPA-I before (black line) and after (red line) grinding and $CHCl_3$ (purple line) and ethyl acetate (EA) (blue line) fuming. (b) photographs of SQDPA-I upon $CHCl_3$ and EA fuming, respectively

In order to understand the different AIE and fluorochromic behavior of these SQDs, single crystals of the four new SQDs were obtained through slow vapor diffusion (Figure S11-S14). All SQDs adopt propeller-like conformations in the single crystal structure, which suggests that the AIE properties might be attributed to the restriction of intramolecular rotations of diphenylamine units.[29] The dihedral angle SQDPA-F between two phenyl groups of the side diphenylamine is 116.41°. The hydrogen bond C-F···H-C length (2.434 Å) of SQDPA-F is shorter than the interaction between hydrogen and other halogen atoms (Figure S11). The drastic friction force might destruct the stronger C-F···H-C interaction of SQDPA-F to cause enhanced emission. The distance of two layers in SQDPA-Cl is 7.389 Å and no halogen bond and C-Cl···H-C interaction was observed between adjacent molecules (Figure S12). Molecular packing of SQDPA-Br molecules was driven by the halogen bonds C-Br···O-C (3.258 Å) and hydrogen bond C-Br···H-C (3.021 Å) in single crystal viewed along the *a* axis (Figure S13). The lack of halogen bonds or the weaker hydrogen bonds make SQDPA-Cl and SQDPA-Br more flexible and easily switch between the crystalline and amorphous states. Molecular packing of SQDPA-I was formed by multiple intermolecular C-I···I-C interactions[30] (3.839 Å, 3.825 Å) and hydrogen bonds C-I···H-C (3.134 Å) in single crystal viewed along the *a* axis (Figure S14). There are more interactions in the case of SQDPA-I than other SQDs and thus endow SQDPA-I with different fluorochromic properties.

In summary, a series of new symmetric squarylium dyes (SQDs) with AIE and flourochromic features were developed. All SQDs display typical AIE behaviour. Among that, SQDPA-F exhibits distinctive mechanofluorochromic properties. While SQDPA-Cl and SQDPA-Br display obvious mechanochromic phoenomenon with high contrast and reversibility. However, SQDPA-I is mechanochromic inactive but possesses obvious vapochromic feature. In contrast, the non-halogen substituted SQDPA-H does not display any flourochromic properties. The photophysical and fluorochromic properties studies reveals that the different halogen substituents greatly influence the eventual functions of these SQDs. Our work demonstrates that incorporating halogen substitution into AIE luminogens provides a new approach for the exploration of novel fluorochromic materials.

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Keywords: symmetric squarylium dyes • halogen • aggregation-induced emission • mechanochromism • vapochromism

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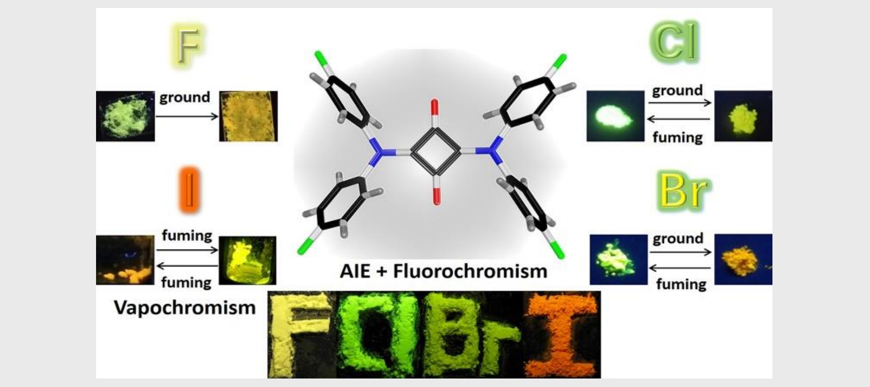

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