### Design and Synthesis of Piezochromic Materials Based on Push–Pull Chromophores: A Mechanistic Perspective

### Fengkun Chen, Jie Zhang, and Xinhua Wan<sup>\*[a]</sup>

Abstract: Computational analysis predicts that intramolecular charge transfer (ICT) exists in anthraquinone imide (AOI) derivatives with electron-donating substituents at the 6-position, such as 4-methoxylphenyl, 4-N,N-dimethylaminophenyl, and thiophene. However, for those with electron-withdrawing ones, no clear ICT interaction could be observed. We predicted, on the basis of the simulation results, that AQI derivatives with electron-donating substituents would be piezochromic. To verify this hypothesis, the corresponding AQI derivatives with various substituents were synthesized. Absorption spectra recorded with a diffuse reflectance method on powders revealed that 4methoxylphenyl-, 4-*N*,*N*-dimethylaminophenyl-, and thiophene-substituted AQI exhibited piezochromism, but not 4-nitrophenyl-substituted AQI, which is in good agreement with the simulation results. Interestingly, redshifts of both the lower and higher energy absorption bands were observed along with red-

**Keywords:** charge transfer • chromophores • donor-acceptor systems • molecular modeling • piezochromic shifts of the emission spectra. However, XRD patterns before and after being pressed presented no significant changes, which was different from known piezochromic molecules described in the literature. An unprecedented mechanism in which enhanced ICT from better conjugation between the donor and acceptor segments induced by the decrease of  $\theta$  under pressure could be responsible for the piezochromism of aryl-substituted AQIs is proposed.

### Introduction

Push-pull chromophores with electron-donor (D) and -acceptor (A) architectures exhibiting intramolecular chargetransfer (ICT) properties have attracted growing interest for both the understanding of fundamental chemistry and physics and promising potential applications in diverse fields, such as organic solar cells,<sup>[1-3]</sup> anion sensors,<sup>[4-6]</sup> nonlinear optics,<sup>[7-10]</sup> and fluorescence imaging.<sup>[11]</sup> One of the most fascinating advantages of such materials is that the  $\pi$  conjugation, band gap, and electro-optical properties could be effectively tuned by judicious choice of the D-A couples,<sup>[12-15]</sup> substituents,<sup>[16,17]</sup> and molecular architectures.<sup>[18]</sup> Such electro-optical properties could also be significantly tuned by disrupting the D-A structures under external stimuli. For example, the optical properties of a series of heteropolycyclic D-π-A fluorescent dyes could be tuned by mechanical stress, which resulted from a phase transition from the crys-

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talline state to a morphous phase induced by the external stress.  $\ensuremath{^{[19]}}$ 

The phenomenon of materials becoming colored under pressure is referred to as piezochromism.<sup>[20]</sup> Polymers, such poly(di-*n*-alkylsilanes)<sup>[21-23]</sup> as and poly(3-alkylthiophene),<sup>[24,25]</sup> transition-metal complexes,<sup>[26-29]</sup> and also some organic dyes<sup>[30-33]</sup> are reported to show piezochromic properties. Due to convenient tunability and easy detection, these functional materials have promising practical applications, such as mechano-sensors, security papers, data storage, and also opto-electronic devices. For most reported piezochromic materials, the phenomenon is mainly explained by perturbations of intermolecular interactions and this is supported by spectroscopic and XRD analyses. For example, as deduced from XRD results, the face-to-face distance in headto-tail-attached poly(octylthiophene) was shortened by 9% after pressing.<sup>[34]</sup> A decrease in the Ni-Ni distance along the c axis from 3.26 Å at ambient pressure to 2.82 Å at high pressure was also believed to lead to the piezochromism of bis(dimethylglyoximato)nickel(II).<sup>[35]</sup> Reversible interconversions between different types of molecular assemblies, as indicated by the disappearance of original reflection peaks or the appearance of new peaks in XRD patterns, have also been testified to induce piezochromism in organic dyes. Kato and Sagara recently reported multiluminescent color switching from a single-luminophore liquid crystal by mechanical stimuli.<sup>[36]</sup> Reversible change between different molecularly assembled structures is considered to contribute to the coloration. Although a variety of piezochromic materials

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have been reported recently, the design principles of piezochromic materials have rarely been reported.<sup>[37]</sup> Recently, we reported a series of anthraquinone imide (AQI)-based molecules with a D-A structure, which changed color from vellow to red when pressed or ground.<sup>[38]</sup> It was found that the lower-energy absorption band exhibiting a redshift under pressure had an intramolecular charge-transfer (ICT) nature and the higher-energy one was assigned to the  $\pi$ - $\pi$ \* transition and also revealed a simultaneous redshift. However, no significant change was observed in the XRD patterns after being pressed. No available mechanism, such as changes of intermolecular interactions or changes in molecular assemblies or chemical reactions,<sup>[30]</sup> is applicable in our case. Therefore, we were motivated to perform in-depth experimental and theoretical investigations on the underlying mechanism of the piezochromism of AQI-containing molecules.

Herein, we provide a new insight into the piezochromic mechanism that is different from those described above. We propose that the origin of piezochromism in aryl-substituted AQIs is enhanced ICT resulting from decreased torsion angles between the electron-donating and -withdrawing segments in the D-A molecules caused by external pressure. To verify this postulation, a series of AQI-based push-pull molecules with electron-donating and -withdrawing substituents were designed with the assistance of prophase computational simulations. For molecules with significant ICT interactions and torsion angles, piezochromic properties were observed, whereas they were absent in molecules without effective intramolecular interactions. Photoluminescence (PL) experiments of the solids illustrated that the emission spectra were also redshifted to a similar extent as that of absorption spectra under pressure. The possibility of the effects of overlapping enhanced intermolecular electronic were also investigated and eventually it was excluded by experimental results from XRD analyses of these compound powders and optical spectroscopic characterization of molecularly dispersed polymer blends of these compounds.

#### **Results and Discussion**

Molecular design by computational simulation: Based on our hypothesis, a series of molecules with diverse substituents (Figure 1), that is, electron-donating ones, such as 4-methoxylphenyl, 4-N,N-dimethylaminophenyl, and thiophene groups, and electron-withdrawing 4-nitrophenyl, were designed to demonstrate the existence of ICT interactions and also to tune the electronic structures. The optimized geometry of each compound was calculated at the B3LYP/6-31G (d, p) level. As shown in Figure 1, there is a dihedral angle between the substituent aryl ring (or thiophene ring) and the rigid planar AQI core in each compound ranges from 20 to 36° due to the subtle balance between two competitive interactions: the o-hydrogen repulsion, which prefers a twisted structure, and  $\pi$ -electron conjugation, leading to a planar structure.<sup>[39]</sup> This moderate angle affords the possibility of pressure-induced torsion around the CC bond between the substituent and the rigid planar core and then regulation of the efficiency of D-A conjugation by external pressure; this is further confirmed by computation results. The energy barriers for transition from twisted to planar structures were estimated to be 5.91 kJ mol<sup>-1</sup> for CH<sub>3</sub>O-Ph-AQI, 4.65 kJ mol<sup>-1</sup> for DMA-Ph-AQI, 6.56 kJ mol<sup>-1</sup> for Nitro-Ph-AQI, and 0.65 kJ mol<sup>-1</sup> for Th-AQI. Such small energy barriers indicate that the D-A molecules are very flexible for the torsional motion from twisted geometries to coplanar ones.<sup>[40]</sup>

The electronic structures and the frontier molecular orbital (MO) energies of each compound were calculated at the same level and are shown in Figure 2. From the electron density distribution of the HOMO and LUMO of CH<sub>3</sub>O-Ph-AQI, it is evident that the largest electron coefficients in the HOMO are located along the whole donating moiety, whereas the coefficients in the LUMO are concentrated on the anthraquinone imide core. This result indicated that upon photoexcitation there might be considerable ICT, which was further verified by time-dependent (TD) DFT results. According to TD-DFT calculations in the gas phase (Table 1), the lowest energy absorption of CH<sub>3</sub>O-Ph-AQI appeared at 523 nm, corresponding to the HOMO–LUMO transition with an oscillator strength (f) of 0.09. The higher energy one was positioned at 362 nm, corresponding to the



Figure 1. Designed AQI derivatives and their optimized geometries. ( $\Phi$ : dihedral angles between the benzene/thiophene ring and anthraquinone core.) DMA-Ph-AQI = *N*-butyl-6-(4-dimethylanilino)anthraquinone-2,3-dicarboxylic imide, CH<sub>3</sub>O-Ph-AQI=*N*-butyl-6-(4-methoxyphenyl)anthraquinone-2,3-dicarboxylic imide, Th-AQI=*N*-butyl-6-(2-thiophenyl)anthraquinone-2,3-dicarboxylic imide, Th-AQI=*N*-butyl-6-(2-thiophe

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Figure 2. The frontier MOs and energies of the AQI derivatives obtained by DFT calculations. HOMO=highest occupied molecular orbital, LUMO=lowest occupied molecular orbital, SUMO=second unoccupied molecular orbital.

tion of CH<sub>3</sub>O-Ph-AQI between the twisted and coplanar geometries (Figure 3), which was in agreement with a decrease in the band gap by 0.14 eV due to better conjugation between the D and A segments. A redshift of the higher energy absorption was observed as well. As shown in Figure 3, the oscillator strength was also enhanced, for example, the oscillator strength of the lower-energy absorption increased from 0.090 to 0.104.

As demonstrated by the calculation results mentioned above, the electronic structures, and ICT properties, could be tuned by varying the substituents on the AQI core. Meanwhile, a decrease in the dihedral angles in all four of the compounds designed could result in redshift of both the higher and lower energy absorptions in molecules with effi-

Table 1.	Absorption	spectra	obtained by	TD-DFT	methods	at the	B3LYP/6-31G(d,p	) optimized	geometries
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Compounds	$\lambda_{\max}^{abs}$ [nm]	f	Main configurations				
	523	0.090	HOMO-0→LUMO+0 (+99%)				
CH <sub>3</sub> O-Ph-AQI	362	0.039	HOMO-0 $\rightarrow$ LUMO+1 (+45%) HOMO-3 $\rightarrow$ LUMO+0 (38%)				
	680	0.101	HOMO- $0 \rightarrow LUMO + 0 (+99\%)$				
DMA-Ph-AQI	425	0.106	HOMO-0 $\rightarrow$ LUMO+1 (+72%) HOMO-0 $\rightarrow$ LUMO+2 (+26%)				
	409	0.244	HOMO-0 $\rightarrow$ LUMO+2 (+73%) HOMO-0 $\rightarrow$ LUMO+1 (26%)				
Th-AQI	495	0.093	HOMO- $0 \rightarrow$ LUMO + 0 (+98%)				
	400	0.006	HOMO-6 $\rightarrow$ L+0 (+81%) HOMO-0 $\rightarrow$ LUMO+0 (+5%)				
Nitro-Ph-AQI	395	0.103	HOMO- $0 \rightarrow$ LUMO+ $0$ (+86%)				
	351	0.042	HOMO-2 $\rightarrow$ LUMO +0 (+83%) HOMO-5 $\rightarrow$ LUMO +0 (+5%)				

cient D–A conjugation. However, due to the disappearance of ICT in Nitro-Ph-AQI, no such redshift could be observed.

**Synthesis:** Schemes 1 and 2 illustrate the synthetic approaches of AQIs with different electron-donating and -withdrawing substituents. 4-Methoxyphenyl and 4-dimethylaminophenyl are electron-do-

 $\pi$ - $\pi^*$  transition (HOMO-0-LUMO+1), and the oscillator strength was 0.039. Similar stimulated optical transitions were obtained for DMA-Ph-AQI and Th-AQI. However, in the case of Nitro-Ph-AQI, the electron density of the HOMO is distributed across the full molecular skeleton and that of the LUMO mainly located at the anthraquinone core, indicating weak ICT. Consequently, the  $\pi$ - $\pi^*$  transition was predicted to appear at a high energy level at around 395 nm.

Interestingly, simulation results also indicated that the absorption of those compounds exhibiting clear ICT showed a dependence on the dihedral angle. For instance, there was a redshift of about 10 nm of the longest-wavelength absorp-



Figure 3. Calculated absorption spectra of  $CH_3O$ -Ph-AQI in twisted and coplanar geometries.

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nating groups; the latter has a stronger donating capacity. 4-Nitrophenyl is an electron-withdrawing substituent. The precursor Br-AQI was synthesized by multistep reactions with a procedure reported by our group.<sup>[38]</sup> Palladium-catalyzed Suzuki coupling reactions were carried out between the Brsubstituted AQI and corresponding phenylboronic acids under standard conditions to afford the products in good yields.



Scheme 1. Synthetic route for AQIs with different phenyl substituents. Br-AQI=6-bromoanthraquinone-2,3-dicarboxylic imide.

The thiophene unit is also an electron-donating substituent with a donating capacity similar to that of the 4-methoxyphenyl group. 5-Methylthiophene-2-boronic acid was initially used to synthesize the thiophene-substituted AQI. Unfortunately, only a byproduct was obtained under the same coupling reaction conditions; this byproduct was further confirmed to be the unsubstituted AQI by <sup>1</sup>H NMR spectroscopy with the loss of the halogen atom (Figure S1 in the Supporting Information). Alternatively, Stille coupling was employed to prepare the thiophene-substituted AQI, as demonstrated in Scheme 2, through a modified synthetic



Scheme 2. Synthetic route for an AQI with a thiophenyl substituent.

route. The coupling reaction was employed before imidization to enhance the solubility of intermediate products. The pure product was obtained as a green-yellow powder in high yield.

The chemical structures of the synthesized AQI derivatives were fully characterized by <sup>1</sup>H NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis. In the <sup>1</sup>H NMR spectra, the chemical shifts of the protons at the benzene ring in CH<sub>3</sub>O-Ph-AQI were located at  $\delta$ =7.73 and 7.07 ppm. When the methoxyl was replaced by *N*,*N*-dimethylanilino, the chemical shifts changed to  $\delta$ =7.71 and 6.87 ppm, indicating a stronger donating capacity of the *N*,*N*-dimethylanilino unit. A low-field shift of the resonances of these protons was observed in the 4-nitrophenyl-substituted AQI Nitro-Ph-AQI, which was consistent with the electron-withdrawing property of the 4-nitrophenyl substituent. The clear splits of the proton

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resonances of the thiophene ring also confirm the chemical structure of Th-AQI.

**Piezochromic properties**: As predicted by simulation results, color changes under external pressure are expected in CH<sub>3</sub>O-Ph-AQI, DMA-Ph-AQI, and

Th-AQI, whereas no clear change is expected for Nitro-Ph-AQI.

To verify our speculation, solid powders of these compounds were pressed or ground with a spoon to investigate the piezochromic properties. As a result, all compounds except Nitro-Ph-AQI exhibited color changes after being pressed, that is, from orange to deep red for CH<sub>3</sub>O-Ph-AQI, dark purple to black for DMA-Ph-AQI, and green–yellow to red for Th-AQI. The color was retained after removal of pressure, but changed reversibly back to the original by redissolving the pressed powder in organic solvents (such as  $CH_2Cl_2$ ) and drying. However, light yellow Nitro-Ph-AQI did not show any significant color change after pressure. The absorption spectra of these compounds before and after the employment of 0.9 GPa of pressure also gives quantitative evidence of the color change (Figure 4). Two bands can



Figure 4. Absorption spectra recorded with a diffuse reflectance method before and after the employment of pressure on a) CH<sub>3</sub>O-Ph-AQI, b) DMA-Ph-AQI, c) Nitro-Ph-AQI, and d) Th-AQI.

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be seen in the spectra shown in Figure 4a, b and d: one in the visible region, corresponding to the observed color, and the other in the ultraviolet region. After pressure (0.9 GPa) was applied, the whole absorption spectrum, including both the peak maximum and the band edge, were redshifted. For compounds with donating substituents, a redshift of about 10 nm in the peak maximum was observed, which was in good agreement with simulation results. The onset of absorption bands displayed even larger redshifts (Table S1 in the Supporting Information), for instance, 69 nm for DMA-Ph-AQI, which may be responsible for the observed significant color changes rather than the redshift of the peak maximum.

Interestingly, piezochromic luminescence was also observed in those piezochromic compounds. As shown in Figure 5, a redshift of 14 nm in the emission peak of CH<sub>3</sub>O-Ph-AQI excited at 310 nm was observed, which was consistent with that of the lowest-energy absorption. Piezochromic

**(a)** 

a and d) c axes.[67]

luminescent materials, which change their fluorescence emission upon external pressure stimuli, have been attracting significant research interest due to the possibility to control fluorescence in solids without chemical modification.<sup>[41,42]</sup>

Crystal structures: The phenomenon that emission spectra change with pressure, that is, piezochromic luminescence, was mainly explained in the literature by modulation of the molecular packing of structures through pressure.[38,43-45] Intuitively, pressure should shorten the distance between adjacent molecules, and consequently, enhance the possibilities of electronic orbital overlap. However, the endogenous require-

ment for such an interaction to dominate is a rather planar molecular architecture and cofacial arrangement.<sup>[35,46]</sup> Single-crystal XRD was employed to get insights into the molecular arrangements in the solid state. The crystal structure and molecular stacking are shown in Figure 6 (see the Supporting Information for more details). There is indeed a torsion angle between the benzene ring and the AQI core (about 8°). Even though it is smaller than the angle (34°) calculated by the molecular simulation in the gas state, a redshift and intensification of the absorptions are also predictable if the molecule twists from the structure with a relatively small angle as 8° to a planar one. In a single-crystal cell, there are four molecules arranged in a herringbone pattern with an intermolecular distance of 3.78 Å (Figure 6b) and a slip angle between two molecules of about 65.5°(Figure 6c, d). For molecules with herringbone stacking structures, the

 $\pi$ - $\pi$  overlap between adjacent molecules is believed to be minimal.<sup>[47–49]</sup>

Because only a few pieces of very thin platelet crystals of compound CH<sub>3</sub>O-Ph-AQI were available, it was not practical to investigate the change of molecular arrangement after pressing by using single-crystal XRD. Instead X-ray powder scattering was used for the powder samples of all compounds. As demonstrated in Figure 7, no significant difference was observed between the X-ray scattering patterns of the Th-AQI powders before and after pressure, except for a negligible shift in the scattering patterns that could be attributed to experimental error. Such a result explicitly excludes the possibility that changes in intermolecular interactions are responsible for piezochromism.

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Figure 5. Emission spectra of CH<sub>3</sub>O-Ph-AQI excited at 310 nm before and after the employment of pressure. (Inset: photograph of the partially





Figure 6. a) Single-crystal X-ray structure of compound CH<sub>3</sub>O-Ph-AQI and stacking patterns along the b) b, c)

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Figure 7. XRD patterns of Th-AQI powders before and after the employment of pressure.

**Characteristic ICT of D–A compounds**: Based on our speculation that ICT of D–A compounds may be responsible for piezochromism, the significant ICT character of these compounds was investigated by UV/Vis absorption spectroscopy in  $CH_2Cl_2$  at room temperature (Figure 8). For compounds



Figure 8. UV/Vis spectra of the AQI derivatives in  $CH_2Cl_2$  (2.5×10<sup>-5</sup> M). TFA = trifluoroacetic acid, TEA = triethylamine.

with electron-donating substituents, multiple absorption bands appear. CH<sub>3</sub>O-Ph-AQI and Th-AQI have almost the same absorption spectra with two bands: one centered at about 310 nm (4.0 eV) and the other at around 420 nm (2.95 eV). The former band can be attributed to a  $\pi$ - $\pi$ \* transition corresponding to the transition between the HOMO and SUMO, as indicated in Table 2, whereas the lowest-energy bands originate from the ICT transitions.<sup>[50,51]</sup> For DMA-Ph-AQI, these two peaks were redshifted to 340 (3.65) and 530 nm (2.34 eV), respectively. This large redshift of the lowest-energy structureless absorption band with the

Table 2.	Calculated	MO	energies	and	corresponding	energy	gaps.
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	HOMO [eV]	LUMO [eV]	SUMO [eV]	$ \Delta E_{\text{L-H}}^{[a]} [\text{eV}]  (\lambda \text{ [nm]}) $	$\frac{\Delta E_{\text{S-H}}^{[b]} [\text{eV}]}{(\lambda [\text{nm}])}$			
CH <sub>3</sub> O-Ph-AQI	-6.08	-3.26	-2.08	2.82 (440)	4.0 (310)			
DMA-Ph-AQI	-5.37	-3.14	-1.96	2.23 (556)	3.41 (364)			
Th-AQI	-6.33	-3.34	-2.23	2.99 (415)	4.10 (305)			
Nitro-Ph-AQI	-7.30	-3.60	-	3.70 (335)	-			
a] L-H=LUMO-HOMO. [b] S-H=SUMO-HOMO.								

stronger donating substituent also illustrates the significant ICT character. The energy gaps of these lowest-energy absorptions are comparable to the estimated energy gaps between the HOMO and LUMO (Table 2).

The ICT absorption character was further confirmed by protonation/neutralization experiments in solutions of DMA-Ph-AQI. The pink solution became almost colorless upon addition of TFA accompanied with the disappearance of the longest-wavelength absorption band, implying that protonation prohibited ICT.<sup>[52]</sup> Upon neutralization with TEA, the original ICT band was regenerated along with the deep color (inset in Figure 8). Similar phenomena have been reported in other push-pull molecules with a N,N-dimethylanilino unit.<sup>[6,53,54]</sup> Deep-colored solids (orange for CH<sub>3</sub>O-Ph-AQI, green-yellow for Th-AQI, and dark purple for DMA-Ph-AQI) could be attributed to the clear ICT-based absorption. No notable ICT absorption of Nitro-Ph-AQI was observed in the visible region due to the lack of effective D-A conjugation and, as a result, the solid is light colored

Furthermore, for molecules with ICT absorptions, the absorbance of the lowest-energy bands in all solvents used (i.e.,  $CH_2Cl_2$ ,  $CHCl_3$ , DMF, toluene, cyclohexane) followed Beer–Lambert law over a 100-fold change in concentration (i.e.,  $10^{-3}$ – $10^{-5}$  M; see Figure S2 in the Supporting Information). Considering the fact that the solutions were saturated at  $10^{-3}$  M and no band shift was observed, no intermolecular interactions existed in solution.<sup>[55]</sup>

Solvent polarity is known to have a great effect on ICT character. To further confirm the ICT nature of the lowestenergy absorption, UV/Vis and PL spectra in solvents with different polarity were recorded. Normalized UV/Vis absorption and fluorescence spectra of Th-AQI in different solvents (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene) are shown in Figure 9. Although the absorption bands show little dependence on the solvent polarity, significant redshifts in the emission spectra with increasing solvent polarity were observed. This relatively large Stokes shift in polar solvents is a typical emission originating from relaxed ICT states. The Lippert–Mataga equation [Eq. (1)] is usually employed to explain the relationship between the Stokes shift and the solvent polarity [Eq. (2)] as follow:<sup>156–58]</sup>

$$\Delta v = v_{\rm abs} - v_{\rm f} = \frac{2\Delta f}{hca} (\Delta \mu)^2 + \text{constant}$$
(1)

$$\Delta f = \frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$$
(2)

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Figure 9. Normalized UV/Vis absorption and fluorescence spectra of Th-AQI in different solvents.

in which  $\Delta v$  is the Stokes shift;  $v_{abs}$  and  $v_f$  are the wavenumbers of absorption and emission peaks, respectively; *h* is Planck's constant; *c* is the speed of light; *a* is the Onsager cavity radius; and  $\Delta \mu = \mu_e - \mu_g$  is the dipole moment difference between the excited and ground states. The orientational polarizability of the solvent ( $\Delta f$ ) could be deduced from the dielectric constant ( $\varepsilon$ ) and the refractive index (*n*) of the solvent, according to Equation (2).

The Lippert relationship in Th-AQI between the Stokes shift and solvent polarities is illustrated in Figure 10. As deduced from Equation (1), the difference in the dipole moment between the ground and excited states could be obtained from the slope of fitted Lippert plot. According to Lippert's suggestion,<sup>[59]</sup> the cavity radius for nonspherical molecules can be approximated to 40 % of their longest axis, considering that the longest axis is estimated to be about 17.4 and 14.7 Å for CH<sub>3</sub>O-Ph-AQI and Th-AQI, respectively, we can conclude a slightly larger change between the



Figure 10. Plot of Stokes shift  $(\Delta v)$  versus the solvent polarity function  $(\Delta f)$  for Th-AQI. Solid lines are the fitted results.

dipole moments of the excited and ground states of  $CH_3O-Ph-AQI$ .

The fluorescence quantum yields of CH<sub>3</sub>O-Ph-AQI and Th-AQI were measured in chloroform and toluene. With the increasing polarities of the solvents from toluene to dichloromethane, the fluorescence quantum yield decreased from 9.1 to 5.4% for Th-AQI and from 12.6% in toluene for CH<sub>3</sub>O-Ph-AQI to completely quenched in dichloromethane. These results are consistent with the expected effects of ICT on fluorescence quantum yield, that is, the fluorescence efficiency should decrease with increasing strength of ICT.<sup>[12]</sup> The completely quenched fluorescence in the case of DMA-Ph-AQI may be attributed to nonradiative energy dissipation and the highly polar excited state.<sup>[60]</sup>

By comparing the emission spectra in Figures 5 and 9, we found that the powder emission spectrum before pressure was similar to that of a dilute solution in nonpolar solvent corresponding to the ICT emission. In crystals of intramolecular D–A compounds, fluorescence emission could result from intramolecular exciplexes, intermolecular exciplexes, and intermolecular excimers due to different interaction pathways between the D and the A.<sup>[61]</sup> However, no other new emission band appeared in the solid state compared with the emission in solution; this would rule out the possibility that emission in the solid state originated from intermolecular excimers.

Mechanism of piezochromism: As predicted by the simulation results, the series of well-designed AQI derivatives with D-A architecture were piezochromic. From results for the crystal structures before and after pressure, the possibility of changes in intermolecular interactions due to shorter molecular distances or crystal structures, which were considered to be the main contributions to piezochromism, would be ruled out. Photo-optical measurements in solution confirmed the ICT nature of the lowest-energy absorption and redshifts of the whole absorption spectra under pressure were illustrated in the solid state. To further verify the fact that the solid emission resulted from intramolecular interactions, but not intermolecular interactions, the absorption and emission spectra of blend films of D-A compounds dispersed in poly(methyl methacrylate) (PMMA) were measured (Figure 11). The concentration (0.05 wt%) was low enough to ensure molecular dispersion.

As shown in Figure 11, the absorption spectrum of Th-AQI in PMMA was the same as that of Th-AQI molecularly dispersed in the nonpolar solvent toluene. As indicated by concentration-dependence results, there were no intermolecular interactions. A slight redshift of the emission spectra in PMMA was observed similar to those in polar solvents, which may result from the larger dielectric constant of PMMA.

When considering the intensification and redshifting of both the absorption and emission bands under pressure, consistent with simulation results, we proposed that the piezochromism of AQI derivatives resulted from the decrease of the torsion angle between the electron-donating and -ac-

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Figure 11. Absorption and emission spectra of Th-AQI dispersed in PMMA (0.05 wt %) and in toluene ( $2.5 \times 10^{-5}$  m).

cepting segments, and thus, more coplanar structures, as illustrated in Figure 12. The pressure-induced coplanarization might lead to better conjugation between the D and A moieties, thus intensifying and redshifting the absorption and emission bands.<sup>[62,63]</sup> In fact, a slight quantum yield increase of 0.2% was also found in the solid state of Th-AQI from 0.3 to 0.5%. Such intramolecular planarization, together with synergetic J-type aggregation, was also employed to explain the enhanced emission of organic fluorescent nanoparticles.<sup>[64]</sup> Therefore, the redshifted absorption and emission, and the slightly enhanced fluorescence intensity, might be attributed to the pressure-induced decrease of the dihedral angle between the D and A moieties, thus leading to enhanced intramolecular coupling or conjugation.



Figure 12. An illustration of the proposed piezochromic mechanism.

#### Conclusion

Based on our previous work on piezochromic D–A molecules, a series of D–A molecules containing AQI moieties with different electron-donating or -withdrawing substituents were designed with the assistance of molecular simulations and prepared to investigate the mechanism of piezochromism in this type of molecule. Compounds with effective ICT interactions exhibit significant color changes under pressure, whereas Nitro-Ph-AQI, which does not have an ICT interaction, does not. Changes in the intermolecular interactions have been proven not to contribute significantly to piezochromism by spectroscopic and X-ray measurements. Intramolecular interactions might be responsible for piezochromism because pressure would induce a decrease in the dihedral angle between the D and A moieties, and consequently, result in better conjugation. Such a mechanism paves the way for exploring diverse piezochromic materials. More significant piezochromism and piezochromic luminescence also could be expected with judiciously designed molecular architectures, such as branched molecules with different D–A geometries, which are under investigation in our lab.

#### **Experimental Section**

**Materials**: 4-Methoxyphenylboronic acid (98%, J&KCHEMICA), 4-nitrophenylboronic acid (97%, J&KCHEMICA), 4-[*N*,*N*-dimethyl-(amino)]phenylboronic acid (98%, Acros), 5-methylthiophene-2-boronic acid (98%, J&KCHEMICA), and 2-(tributylstanyl)thiophene (97%, Aldrich) were used as purchased. Br-AQI was synthesized by following the procedure reported previously.<sup>[65]</sup> [Pd(PPh<sub>3</sub>)<sub>4</sub>] was synthesized in our laboratory. DMF was purified by distillation under vacuum and stored over 4 Å molecular sieves prior to use. Other solvents and reagents were commercially available and used without further purification unless otherwise specified.

Synthesis of DMA-Ph-AQI: Br-AQI (0.4745 g, 1.15 mmol), 4-[N,Ndimethyl(amino)]phenylboronic acid (0.2089 g, 1.27 mmol), NaHCO3 (0.4 g, 4.76 mmol), and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (20 mg, 0.018 mmol) were added to a 50 mL three-necked round-bottomed flask fitted with a magnetic stirrer bar and a condenser. After being degassed and refilled with nitrogen three times, benzene (20 mL), ethanol (5 mL), and distilled water (10 mL) were added under nitrogen. Then, the mixture was heated to reflux for 4 h. After cooling, the reaction mixture separated into two phases. The organic layer was isolated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×30 mL). The combined organic layer was washed successively with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (with CH2Cl2 as eluent) to give DMA-Ph-AQI (0.4678 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.79$  (s, 2H), 8.54 (d, J=3.5 Hz, 1 H), 8.37 (d, J=8.2 Hz, 1 H), 8.06 (q,  $J_1=8.2$ ,  $J_2=1.9$  Hz, 1H), 7.72 (d, J=8.8 Hz, 2H), 6.88 (br, 2H), 3.79 (t, J=7.3 Hz, 2H), 3.07 (s, 6H), 1.73-1.69 (m, 2H), 1.43-1.37 (m, 2H), 0.99 ppm (t, J=7.3 Hz,

3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =182.0, 181.1, 166.8, 166.7, 147.5, 138.4, 138.2, 135.9, 135.6, 133.5, 131.4, 130.3, 128.6, 128.2, 124.3, 122.4, 112.8, 40.5, 38.4, 30.5, 20.1, 13.6 ppm; HRMS: *m/z* calcd for C<sub>28</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> [*M*+H]<sup>+</sup>: 453.1814; found: 453.1821; elemental analysis calcd (%) for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: C 74.32, H 5.35, N 6.19; found: C 74.52, H 5.45, N 6.21.

**Synthesis of CH<sub>3</sub>O-Ph-AQI**: CH<sub>3</sub>O-Ph-AQI was synthesized in 87% yield by a similar method to DMA-Ph-AQI. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =8.80 (d, *J*=1.7 Hz, 2H), 8.55 (d, *J*=1.9 Hz, 1H), 8.41 (d, *J*=8.1 Hz, 1H), 8.07 (q, *J*<sub>1</sub>=8.1, *J*<sub>2</sub>=1.9 Hz, 1H), 7.72 (d, *J*=8.8 Hz, 2H), 7.06 (d, *J*=8.8 Hz, 2H), 3.90 (s, 3H), 3.80 (t, *J*=7.3 Hz, 2H), 1.75–1.67 (m, 2H), 1.43–1.37 (m, 2H), 0.99 ppm (t, *J*=7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =181.8, 181.2, 166.6, 160.8, 147.3, 138.3, 138.2, 136.0, 135.9, 133.6, 132.3, 131.1, 130.9, 128.6, 125.2, 122.5, 114.8, 55.5, 38.5, 30.5, 20.1, 13.6 ppm; HRMS: *m*/z calcd for C<sub>27</sub>H<sub>22</sub>NO<sub>5</sub> [*M*+H]<sup>+</sup>: 440.1498; found: 440.1497; elemental analysis calcd (%) for C<sub>27</sub>H<sub>21</sub>NO<sub>5</sub>: C 73.79, H 4.82, N 3.19; found: C 73.75, H 5.00, N 3.17.

**Synthesis of Nitro-Ph-AQI**: Nitro-Ph-AQI was synthesized in 33 % yield by a similar method to DMA-Ph-AQI. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 8.83 (d, J=2.2 Hz, 2 H), 8.63 (d, J=1.7 Hz, 1 H), 8.52 (d, J=8.1 Hz, 1 H), 8.42 (d, J=8.7 Hz, 2 H), 8.15 (q,  $J_1$ =8.1,  $J_2$ =1.7 Hz, 1 H), 7.92 (d, J= 8.7 Hz, 2 H), 3.80 (t, J=7.3 Hz, 2 H), 1.75–1.68 (m, 2 H), 1.43–1.37 (m, 2 H), 0.99 ppm (t, J=7.3 Hz, 3 H); HRMS: m/z calcd for  $C_{26}H_{19}N_2O_6$  [M+H]<sup>+</sup>: 455.1243; found: 455.1238; elemental analysis calcd (%) for  $C_{26}H_{18}N_2O_6$ : C 68.72, H 3.99, N 6.16; found: C 68.79, H 4.26, N 6.05.

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**Synthesis of Th-AQI**: Diethyl 6-bromo-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylate (0.6468 g, 1.5 mmol) and  $[Pd(PPh_3)_4]$  (170 mg, 0.153 mmol) were added to a 100 mL three-necked round-bottomed flask fitted with a magnetic stirrer bar and a condenser. After being degassed and refilled with nitrogen three times, anhydrous DMF (15 mL) and 2-(tributylstanyl)thiophene (0.6 g, 1.6 mmol) were added under nitrogen. The mixture was stirred at 80°C for 24 h. After the removal of DMF under vacuum, the resulting solid was purified by column chromatography on silica gel (with  $CH_2Cl_2$  as eluent) in a yield of about 92%.

This solid (0.6 g), together with KOH (4 g) and a mixture of ethanol and water (60 mL, v/v: 1/2), were added to a 250 mL flask and the mixture was heated to reflux overnight. The mixture was acidified with dilute hydrochloric acid solution to pH $\approx$  2. The solid that precipitated was filtered, washed with water, and dried to afford the hydrolysate (0.5 g, 95%).

The hydrolysate (0.5 g) and acetic anhydride (30 mL) were added to a 50 mL round-bottomed flask. The mixture was heated to reflux overnight and then cooled to room temperature. 6-Thiophenylanthraquinone-2,3-dicarboxylic anhydride was obtained after filtration and was washed with petroleum ether (0.44 g, yield 93 %).

6-Thiophenylanthraquinone-2,3-dicarboxylic anhydride (0.44 g, 1.22 mmol) was added to a 50 mL three-necked flask. After being degassed and refilled with nitrogen three times, n-butylamine (0.134 g, 1.83 mmol) and anhydrous DMF (15 mL) were added. After being stirred for 1 h at room temperature, the mixture was heated to reflux for 12 h. The mixture was allowed to cool to room temperature. After the removal of DMF under vacuum, the product was purified by chromatography on silica gel (with CH2Cl2 as eluent) to afford Th-AQI (0.42 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.80$  (d, J = 1.8 Hz, 2H), 8.56 (d, J =1.9 Hz, 1H), 8.38 (d, J = 8.2 Hz, 1H), 8.08 (q,  $J_1 = 8.2$ ,  $J_2 = 1.9$  Hz, 1H), 7.64 (d, J=3.5 Hz, 1 H), 7.50 (d, J=5.0 Hz, 1 H), 7.21 (q,  $J_1=5.1$ ,  $J_2=$ 3.7 Hz, 1 H), 3.80 (t, J=7.3 Hz, 2 H), 1.75-1.65 (m, 2 H), 1.43-1.37 (m, 2H), 0.99 ppm (t, J = 7.3 Hz, 3H); HRMS: m/z calcd for  $C_{24}H_{18}NO_4S$  $[M+H]^+$ : 416.0957; found: 416.0954; elemental analysis calcd (%) for C<sub>24</sub>H<sub>17</sub>NO<sub>4</sub>S: C 69.38, H 4.12, N 3.37; found: C 69.38, H 4.32, N 3.32.

**Instruments and measurements:** <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker ARX400 (400 MHz) spectrometer at ambient temperature with CDCl<sub>3</sub> as the solvent. Chemical shifts ( $\delta$ ) were recorded in ppm with tetramethylsilane as the internal standard. High-resolution mass spectra were recorded on a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer. Elemental analyses were performed on an Elementar Vario EL instrument.

UV/Vis absorption spectra were recorded on a Perkin–Elmer lambda 35 spectrophotometer. PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Diffuse reflectance measurements on powders were carried out on a Shimadzu UV-3100 UV/Vis/NIR spectro-photometer. XRD spectra were examined by using a high-flux SAXS instrument (SAXSess, Anton Paar) equipped with a Kratky block-collimation system and an imaging plate (IP) as the detector. Single-crystal XRD experiments were performed at the Beijing Synchrotron Radiation Facility.

**Computational details**: The ground-state geometries were fully optimized without any symmetry constraints at the DFT level with the Gaussian 09 package,<sup>[66]</sup> using the B3LYP functional and the 6-31G(d, p) basis set. Following each optimization, the vibrational frequencies were calculated to make sure that all optimized structures were stable geometric structures. The frontier MO energy level distributions were estimated at the same functional level based on the optimized structures without zeropoint energy corrections. TD-DFT was employed to stimulate optical properties with the B3LYP/6-31+G(d,p) basis set. To shorten the time required for computation processes, the butyl group was replaced with a methyl group in all simulations, which was not considered to affect the calculations.

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