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Supporting information

Heteroatom induced contrasting effects on the stimuli responsive properties of anthracene based donor-π-acceptor fluorophores

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Table of contents

Scheme S1: Synthesis of **ABO** and **ABT**

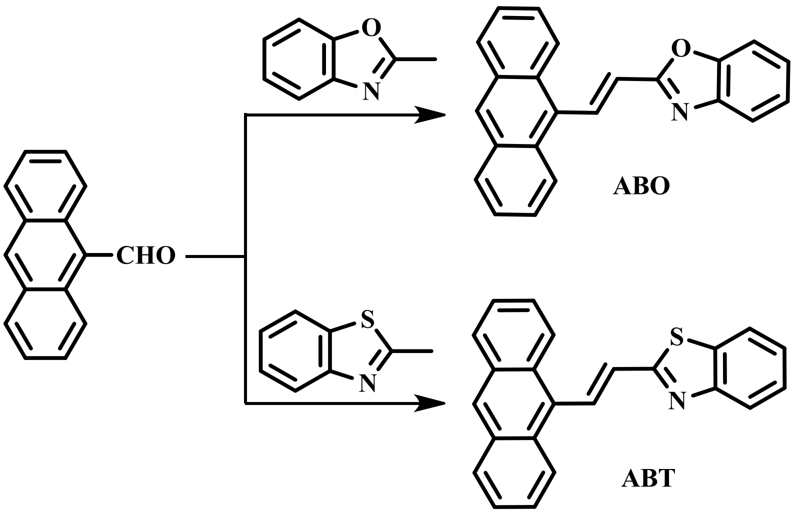
Table S1: Crystal data and structure refinements of **ABO** and **ABT** crystals.

Fig. S1: PXRD pattern of **ABO** and **ABT** under pristine, ground and recovered states.

Fig. S2: ^{1}H NMR spectra of **ABO** in the absence and presence of TFA.

Fig. S3: ^{1}H NMR spectra of **ABT** in the absence and presence of TFA.

Fig. S4: PXRD pattern of **ABO** and **ABT** under pristine, fumed with TFA and recovered states.



Scheme S1: Synthesis of **ABO** and **ABT**; *Reagents and conditions*: *t*-BuOK, 0 °C, dry THF, 2h.

Table S1: Crystal data and structure refinements of two crystals

Parameters	**ABO**	**ABT**
Empirical formula	$C_{23}H_{15}NO$	$C_{23}H_{15}NS$
Formula mass	321.36	337.42
T, K	301(2)	293 (2)
Crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	9.805 (15)	9.853 (14)
b, Å	13.501(18)	14.006 (19)
c, Å	13.18 (2)	12.99 (2)
α,deg	90	90
β,deg	106.35 (3)	107.08 (2)
γ,deg	90	90
V, Å^3	1674 (4)	1714 (4)
Z	4	4
density, mg/m^3	1.275	1.308
λ (Mo K_α) Å	0.71073	0.71073
μ, mm^{-1}	0.078	0.193
θ range, deg	3.0 to 27.5	3.1 to 27.4
no. of reflections collected	13498	12541
no. of unique reflections	3387	3390
F(000)	672	704
GOF	0.759	1.120
R1	0.0610	0.0811
wR2	0.1466	0.2107

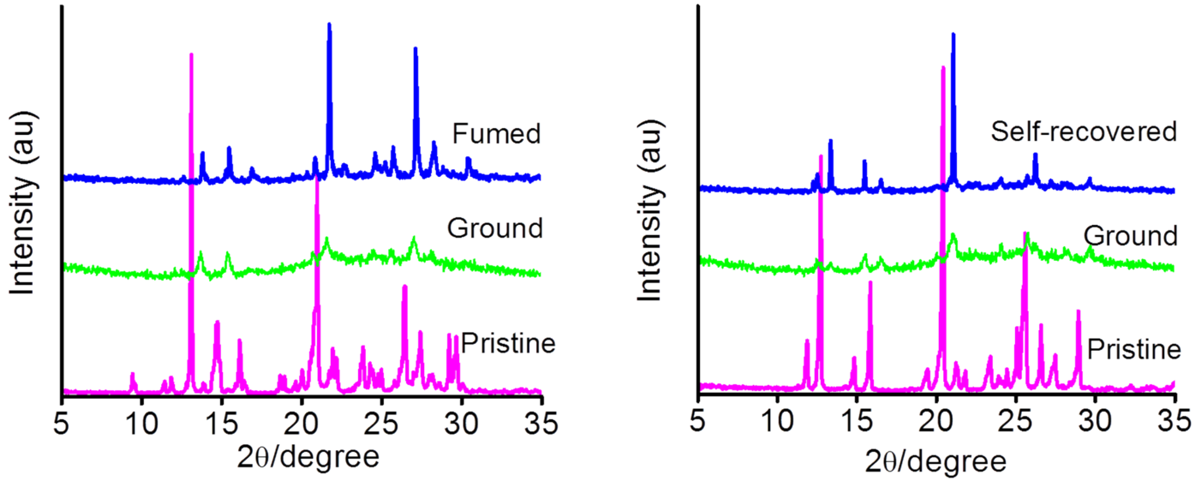


Fig. S1 PXRD pattern of a) **ABO** and b) **ABT** under different conditions.

The fluorescence changes on applying mechanical stimuli in both cases could be attributed to the destruction of the ordered packing of molecules leading to an amorphous state, and the subsequent modulation of the chromophore interactions. In order to prove this mechanism, the powder X-ray diffraction (PXRD) patterns of the molecules under various conditions was investigated (**ABO**: pristine, ground and solvent fumed; **ABT**: pristine, ground and self-recovered, Figure S1). The pristine samples exhibited sharp and intense diffractions implying crystalline nature of the materials. On the other hand, the diffraction peaks were weak and broad for ground samples indicating an amorphous nature. The recovered samples again exhibited sharp and intense peaks indicating the reversal to the ordered chromophore organization. However, the peak pattern was different from the pristine samples indicating the exact crystalline packing of the pristine state is not achieved on recovery. Nevertheless, the reversal of the chromophore organization at the molecular level would be enough to restore original emission properties.

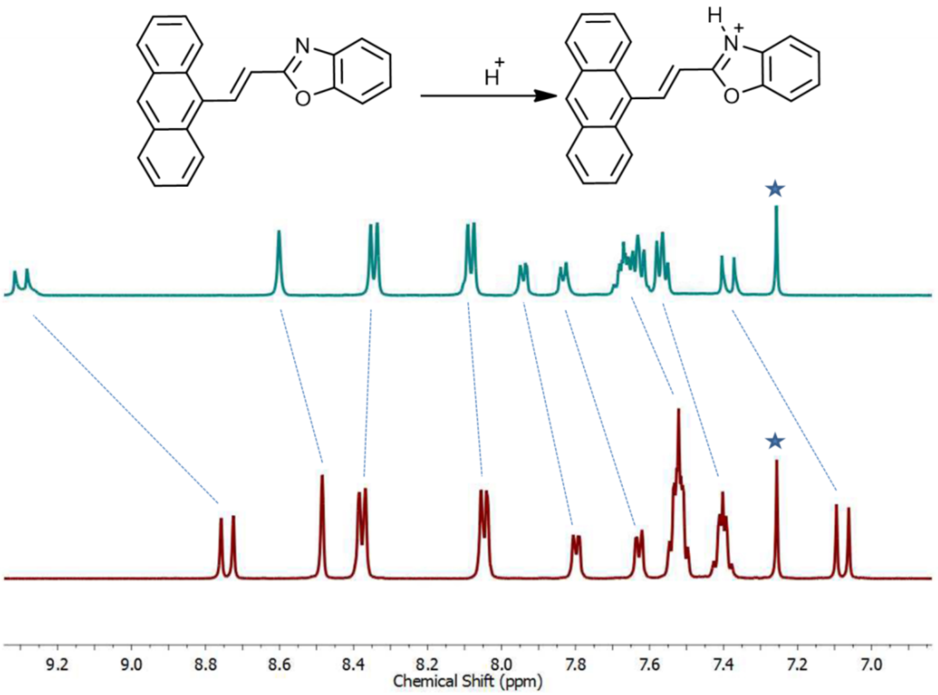


Fig. S2: ^{1}H NMR spectra of **ABO** in the absence (down) and presence (top) of 10 equiv. of TFA in $CDCl_3$.

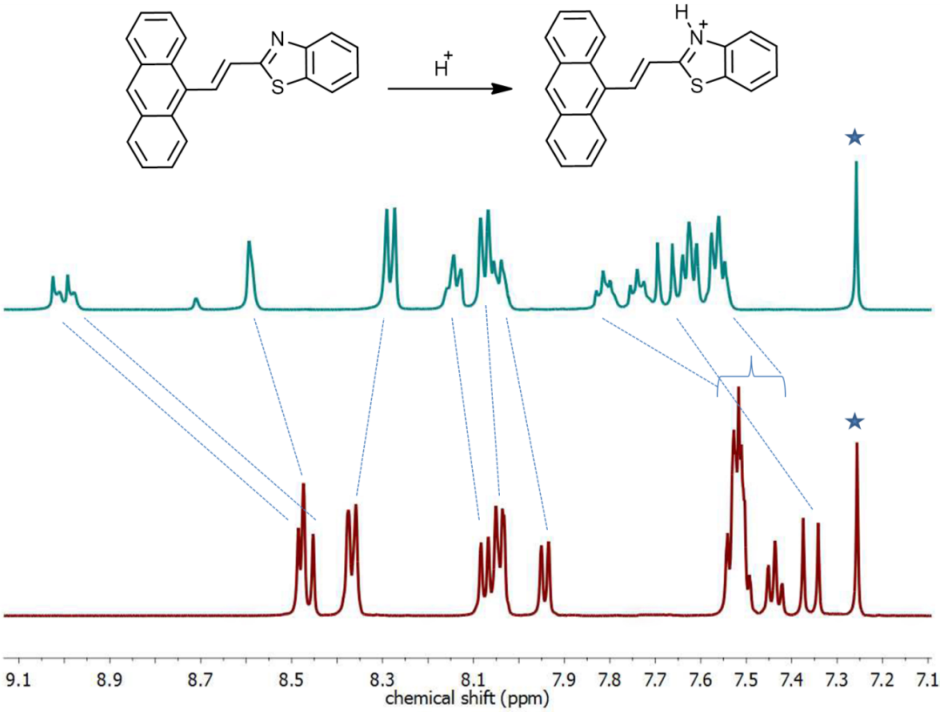


Fig. S3: ^{1}H NMR spectra of **ABT** in the absence (down) and presence (top) of 10 equiv. of TFA in $CDCl_3$.

^{1}H NMR spectra of **ABO** (Fig. S2) and **ABT** (Fig. S3) in the absence and presence of TFA is analyzed for confirming the interaction of these molecules with TFA. The comparison showed significant down-field shift for vinylic protons and most of the aromatic protons on addition of TFA. This implies protonation on the nirogen atom of the benzoxazole/benzothiazole moiety leading to the decrease of electron density in the vicinity of these protons.

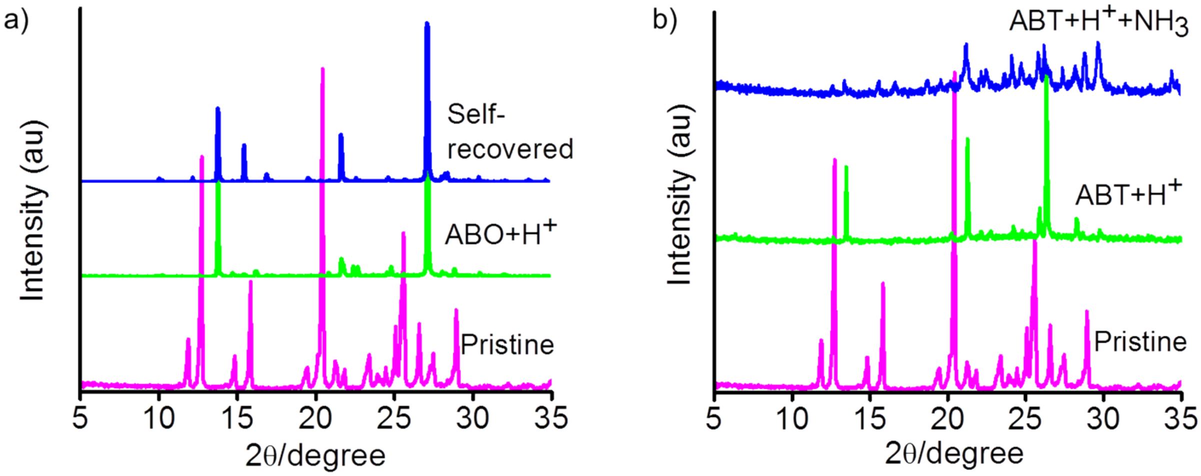


Fig. S4: PXRD pattern of a) **ABO** and b) **ABT** under different conditions.

It is known that TFA has the ability to dissolve organic compounds, and the resulting morphological changes can induce color changes. To verify this possibility in the present case, XRD pattern of the compounds were analyzed under various conditions (**ABO**: pristine, fumed with TFA and self-recovered, Fig. S4a; **ABT**: pristine, fumed with TFA and recovered on ammonia exposure, Fig. S4b). The change in crystallinity/morphology due to dissolution of the materials in presence of TFA was evident from the XRD pattern. However, the recovered samples (which show the same emission properties as that of pristine materials) do not have the same XRD pattern as that of pristine materials. This clearly indicates that the color change upon exposure to TFA is not due to the morphology change, whereas, it is due to the protonation process.