Electronic Supplementary Information

Photoinduced structural changes of cationic azo dyes confined in two dimensional nanospace by two different mechanisms

by

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Characterization of AzNaph

Chemical Formula: C_{21}H_{24}N_{3}O^{+}

Exact Mass: 334.19
Molecular Weight: 334.44
m/z: 334.19 (100.0%), 335.20 (23.0%), 336.20 (2.7%), 335.19 (1.1%)

ESI-MS: Thermo Finnigan / LCQ

^1^H NMR (300 MHz, DMSO) δ 8.86 (d, J = 8.2 Hz, 1H), 8.18 – 8.02 (m, 4H), 7.83 – 7.58 (m, 4H), 7.26 (d, J = 9.0 Hz, 2H), 4.63 (s, 2H), 3.94 – 3.81 (m, 2H), 3.23 (s, 9H).
Bruker / Avance-300

^1^3^C NMR (125 MHz, DMSO) δ 160.16, 147.35, 146.70, 133.93, 131.12, 130.39, 128.10, 127.15, 126.68, 125.85, 124.88, 122.81, 122.39, 115.48, 114.63, 111.56, 63.98, 62.12, 53.11.
Bruker / Avance-500
Calculation of volume occupying azo dyes in the interlayer space

Occupation volume of the cationic azo dye in the interlayer space of magadiite (per Si$_{14}$O$_{29}$ unit) was obtained by dividing the volume of intercalated azo dye (1) by the volume of the interlayer space (2).

(1) Volume of intercalated azo dye = (amount of the adsorbed cationic dye)×(the molecular volume [nm$^3$])

- AZ$^+$-magadiite: (1.8 mol / Si$_{14}$O$_{29}$)×(0.262 nm$^3$) = 0.472 nm$^3$/Si$_{14}$O$_{29}$
- AzNaph$^+$-magadiite: (0.85 mol / Si$_{14}$O$_{29}$)×(0.335 nm$^3$) = 0.285 nm$^3$/Si$_{14}$O$_{29}$

(2) the volume of the interlayer space = (ideal surface area of magadiite 0.547 nm$^2$/Na$_2$Si$_{14}$O$_{29}$)$^1$×(the gallery height [nm])

- AZ$^+$-magadiite: (0.547 nm$^2$/Na$_2$Si$_{14}$O$_{29}$)×(1.62 nm) = 0.886 nm$^3$/Si$_{14}$O$_{29}$
- AzNaph$^+$-magadiite: (0.547 nm$^2$/Na$_2$Si$_{14}$O$_{29}$)×(1.89 nm) = 1.03 nm$^3$/Si$_{14}$O$_{29}$


Occupation volume of azo dye in the interlayer space is

- AZ$^+$-magadiite: (0.472/0.886)×100 = 53%
- AzNaph$^+$-magadiite: (0.472/1.03)×100 = 28%
Fig. S1. XRD patterns of (a) trans-AZ$^+$- and (b) trans-AzNaph$^+$-magadiite recorded under different humidity of RH = 10, 50, and 90%.