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Electronic Supplementary Information

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

by

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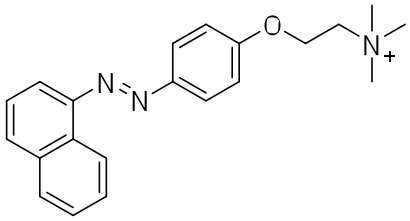
Characterization of AzNaph$^+$



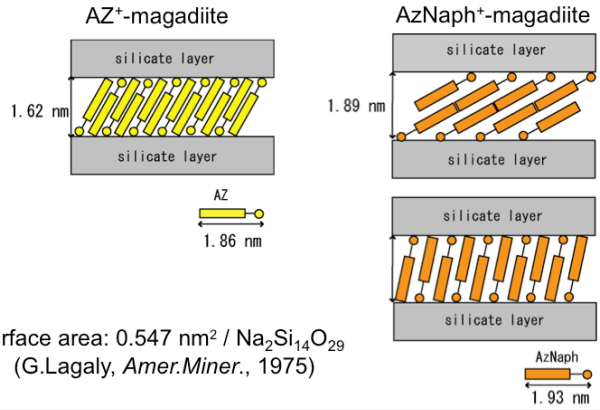
Chemical Formula: $C_{21}H_{24}N_3O^+$
Exact Mass: 334.19
Molecular Weight: 334.44
m/z: 334.19 (100.0%), 335.20 (23.0%), 336.20 (2.7%), 335.19 (1.1%)

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

^{13}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



Surface area: 0.547 nm^2 / $Na_2Si_{14}O_{29}$
(G.Lagaly, *Amer.Miner.*, 1975)

	AZ^+	$AzNaph^+$
Amount of adsorbed dye	1.8 mol / $Si_{14}O_{29}$	0.85 mol / $Si_{14}O_{29}$
Molecular volume	0.262 nm^3	0.335 nm^3
Occupation volume	53%	28%

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 /$Si_{14}O_{29}$)×(0.262 nm^3) = 0.472 $nm^3/Si_{14}O_{29}$
- $AzNaph^+$-magadiite: (0.85 /$Si_{14}O_{29}$)×(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 $nm^2/Na_2Si_{14}O_{29}$)[*1]×(the gallery height [nm])

- AZ^+-magadiite: (0.547 $nm^2/Na_2Si_{14}O_{29}$)×(1.62 nm) = 0.886 $nm^3/Si_{14}O_{29}$
- $AzNaph^+$-magadiite: (0.547 $nm^2/Na_2Si_{14}O_{29}$)×(1.89 nm) = 1.03 $nm^3/Si_{14}O_{29}$

*1: Lagaly, G.; Beneke, K. Weiss, A. *Am. Miner.* **1975,** *60,* 642.

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%**

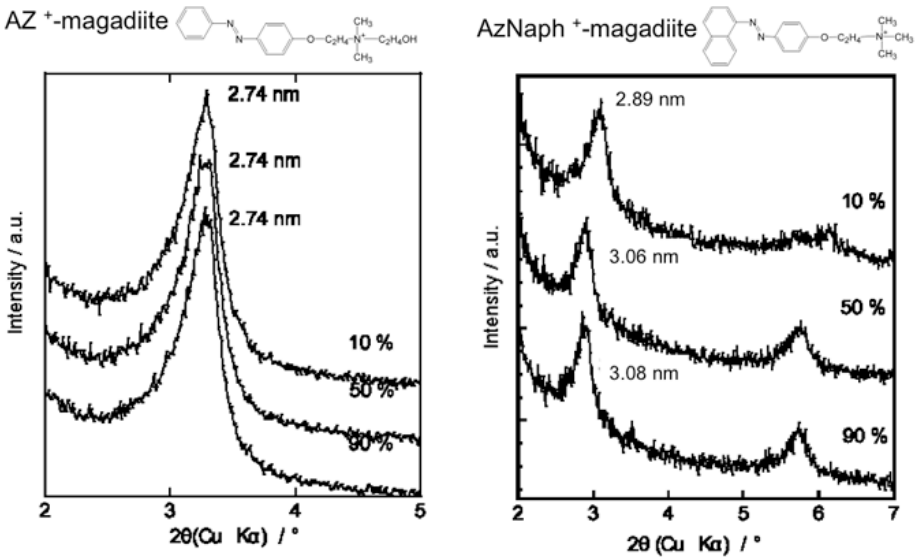


Fig. S1. XRD patterns of (a) *trans*-AZ^+- and (b) *trans*-$AzNaph^+$-magadiite recorded under different humidity of RH = 10, 50, and 90%.