Supporting Information

Dense Integration of Stable Aromatic Radicals within the Two-dimensional Interlayer Space of Clay Minerals via Clay-Catalyzed Deamination of Arylammoniums

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Contents:

1. Microscopic images of SA reacted with 1AA

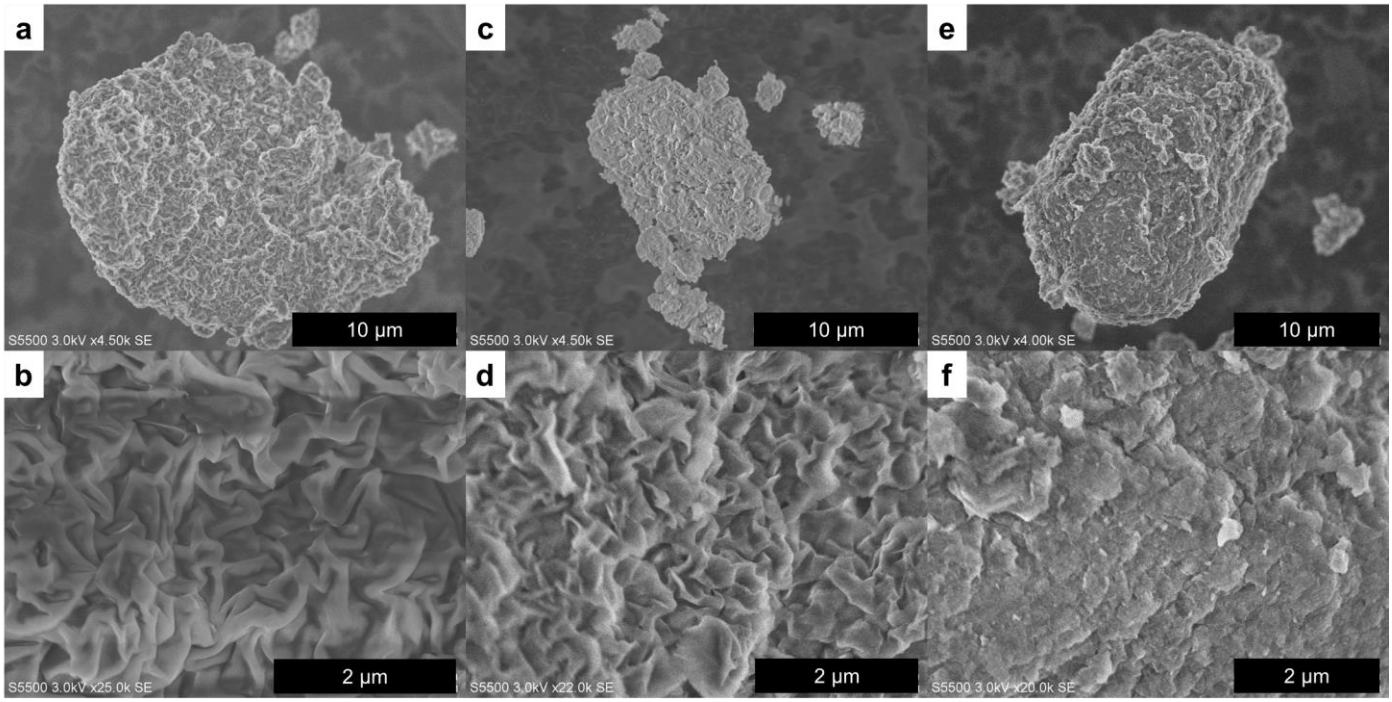

Figure S1. SEM images of (a, b) pristine SA, (c, d) 1AA_SA_RT, and (e, f) 1AA_SA_reflux.

2. Confirmation of deamination of 1AA from its reaction with SA

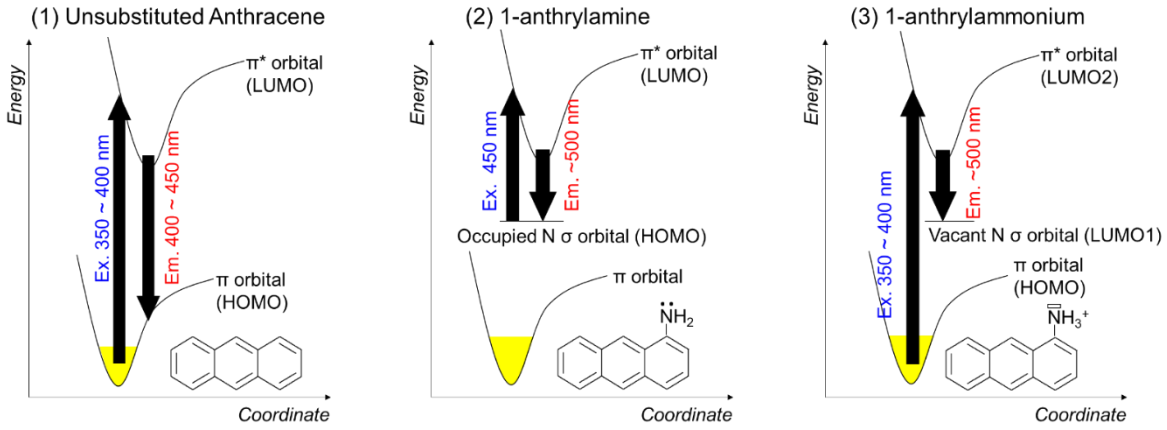

Figure S2. Energetic profiles of emission process in anthracene derivatives. In (1), unsubstituted anthracene, emission and excitation spectra reflect the π orbital (HOMO) and π* orbital (LUMO), while in the case of (2), 1-anthrylamine, the occupied N σ orbital standing between the π and π* orbital predominates their excitation and emission spectra. In (3), 1-anthrylammonium, although the N σ orbital is vacant due to ionization, N σ orbital affects their emission spectra. Thus, the deamination of 1-anthrylammonium (or 1-anthrylamine) can be easily confirmed by emission-excitation spectroscopy.

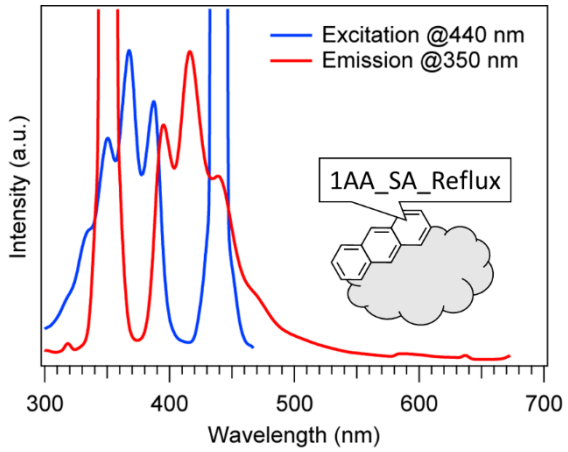

Figure S3. Excitation-emission spectra of 1AA_SA_Reflux. The emission spectrum was measured under λ = 350 nm excitation light, while the excitation spectrum was recorded under λ = 440 nm light emission.

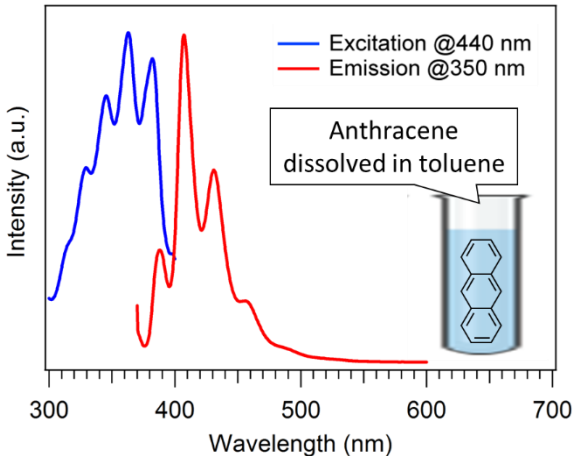

Figure S4. Excitation-emission spectra of anthracene dissolved in toluene (1 mM). The emission spectrum was measured under λ = 350 nm excitation light, while the excitation spectrum was recorded under λ = 440 nm light emission.

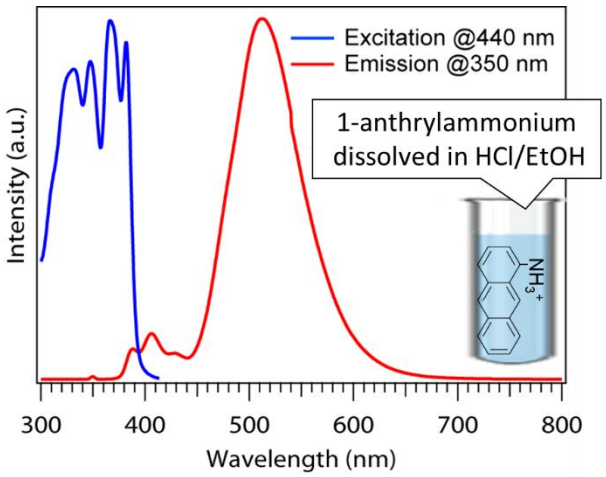

Figure S5. Excitation-emission spectra of 1-anthrylammonium dissolved in 1:1 vol% 1M HCl/EtOH (1 mM). The emission spectrum was measured under λ = 350 nm excitation light, while the excitation spectrum was recorded under λ = 440 nm light emission.

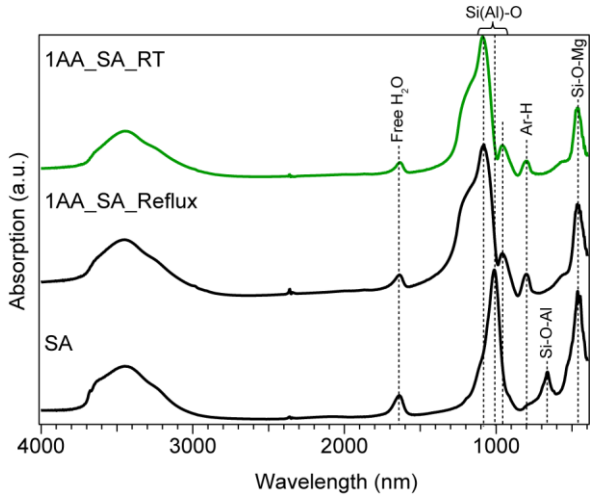

Figure S6. FT-IR spectra of parent SA, 1AA_SA_Reflux, and 1AA_SA_RT.

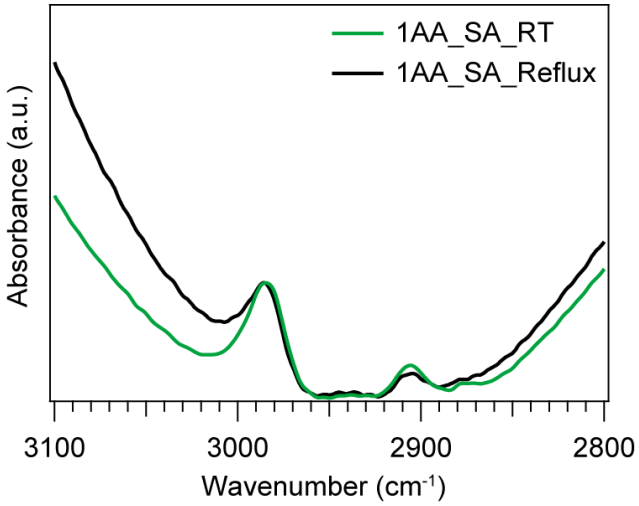

Figure S7. The enlarged FT-IR of the spectra shown in Figure S5.

3. Demonstration of CCD for anthracene radical cation formation within MMT

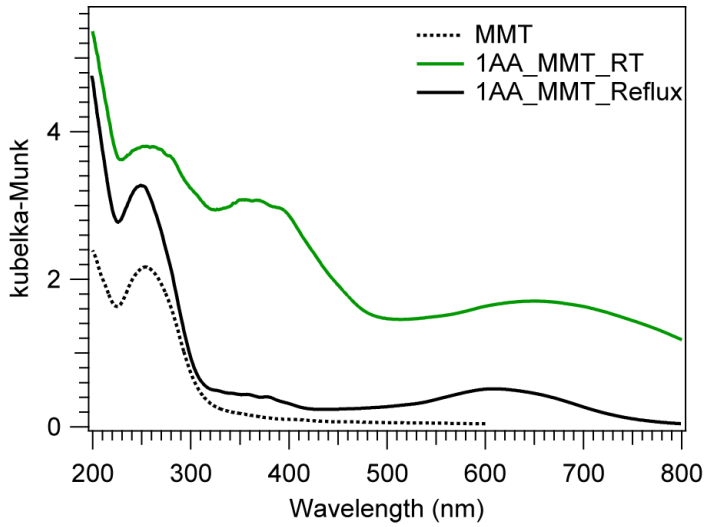

Figure S8. Diffuse reflectance spectra of MMT reacted with 1AA. Reaction conditions: MMT (1 g), 1AA (0.2 mmol), EtOH (100 mL), and 1M HCl (100 mL) at RT or reflux (120 °C), 24 h.

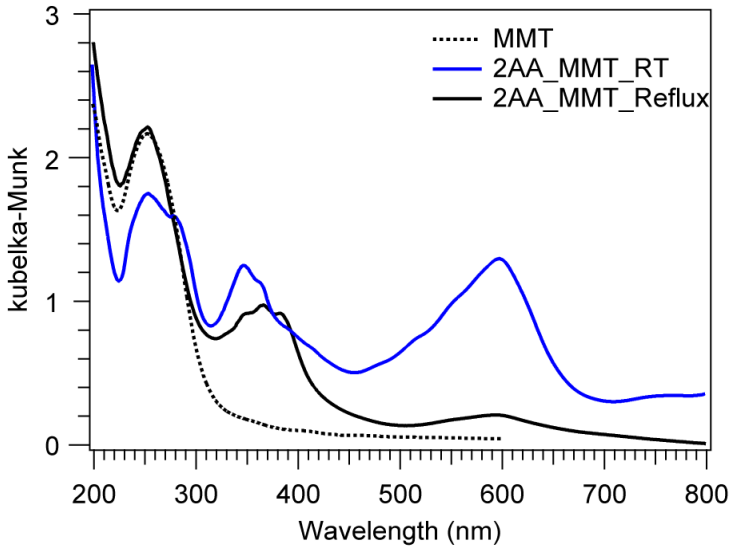

Figure S9. Diffuse reflectance spectra of MMT reacted with 2AA. Reaction conditions: MMT (1 g), 2AA (0.2 mmol), EtOH (100 mL), and 1M HCl (100 mL) at RT or reflux (120 °C), 24 h.

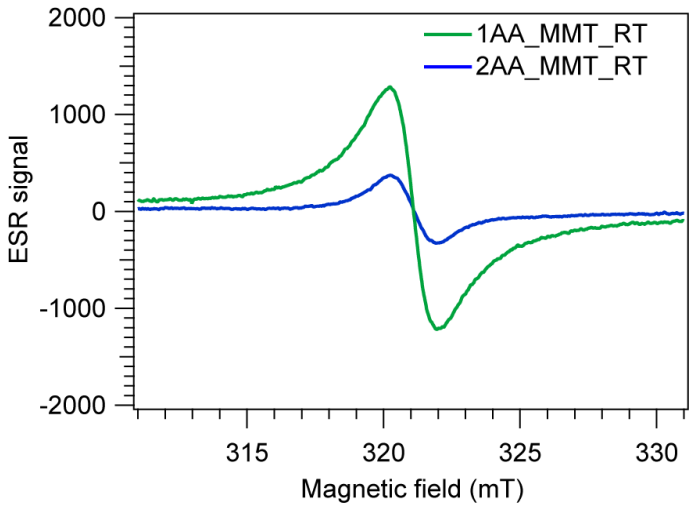

Figure S10. X-band ESR spectra of MMT reacted with 1AA or 2AA.

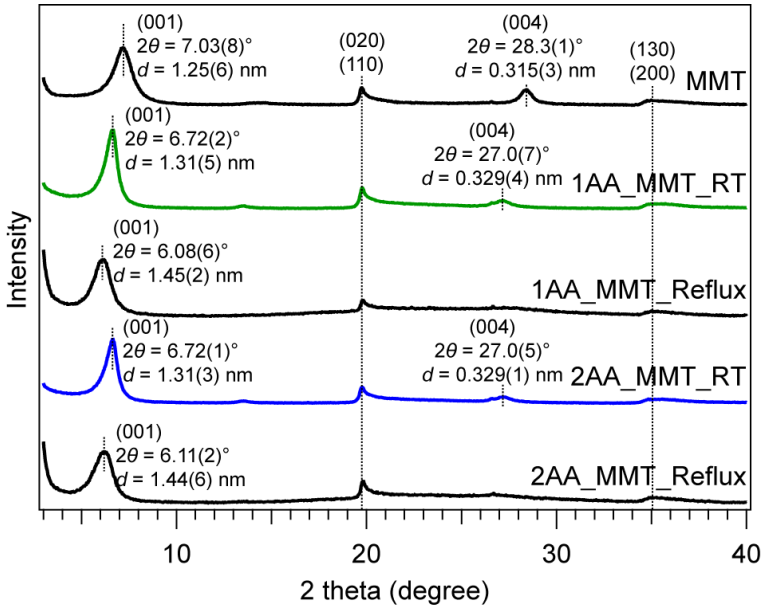

Figure S11. XRD patterns of MMT reacted with 1AA or 2AA.

4. Reaction time course of SA with anthrylammoniums

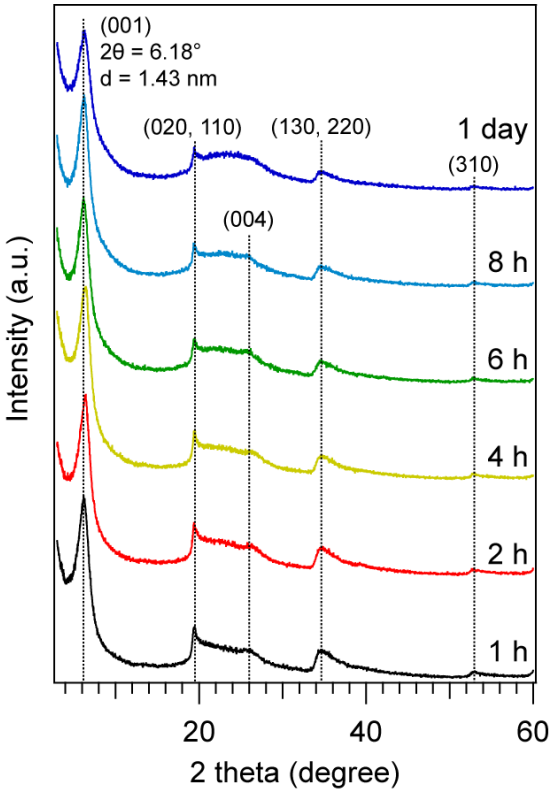

Figure S12. Time course of XRD patterns of SA reacted with 1AA. Reaction conditions: SA (1 g), 1AA (0.2 mmol each), EtOH (100 mL) and 1M HCl (100 mL) at RT.

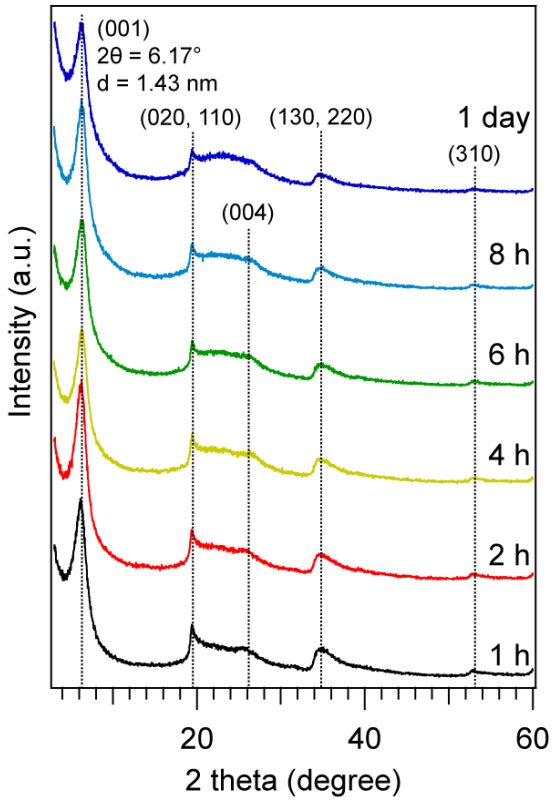

Figure S13. Time course of XRD patterns of SA reacted with 2AA. Reaction conditions: SA (1 g), 2AA (0.2 mmol each), EtOH (100 mL) and 1M HCl (100 mL) at RT

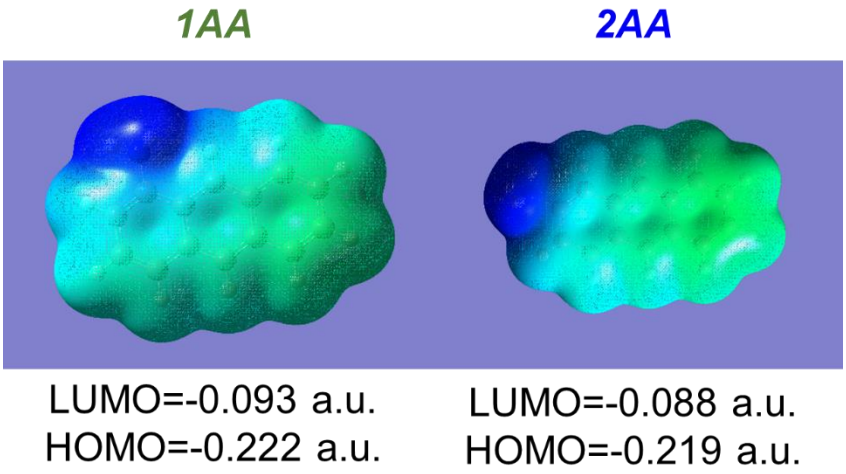

Figure S14. DFT calculated potential mapping of 1AA and 2AA.

5. Application of CCD using naphthylammonium with various substituents

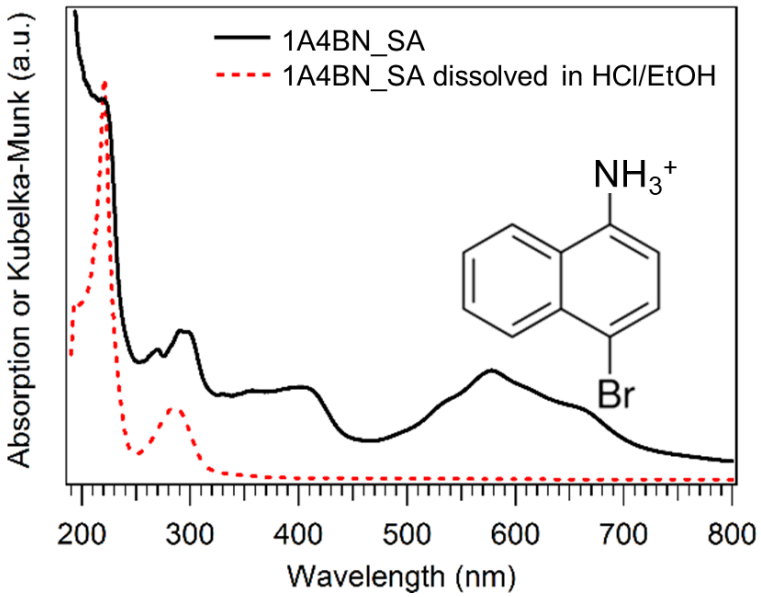

Figure S15. Transmittance absorption spectrum of 1 mM 1-ammonium-4-bromonaphthalene (1A4BN) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 1A4BN (solid). Reaction conditions: SA (1 g), 1A4BN (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

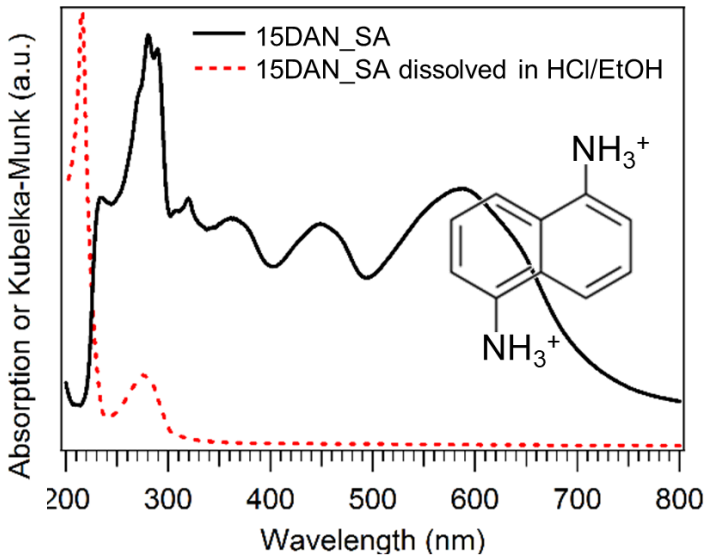

Figure S16. Transmittance absorption spectrum of 1 mM 1,5-diammoniumnaphthalene (15DAN) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 15DAN (solid). Reaction conditions: SA (1 g), 15DAN (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

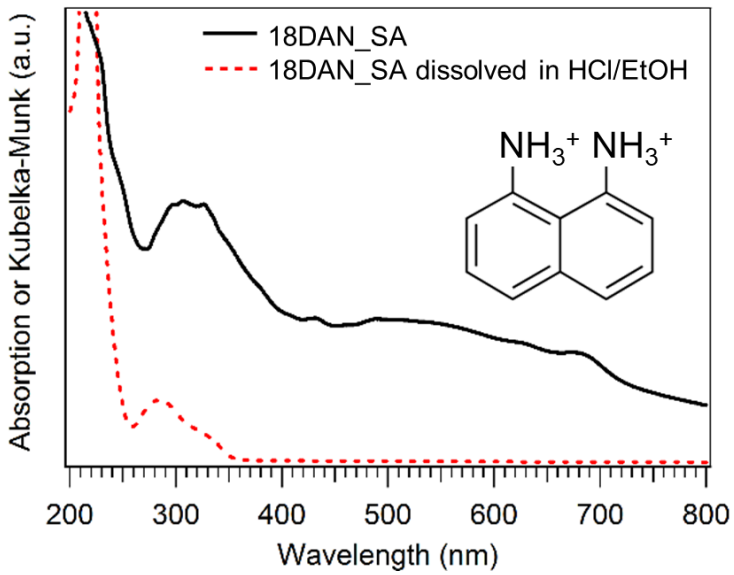

Figure S17. Transmittance absorption spectrum of 1 mM 1,8-diammoniumnaphthalene (18DAN) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 18DAN (solid). Reaction conditions: SA (1 g), 18DAN (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

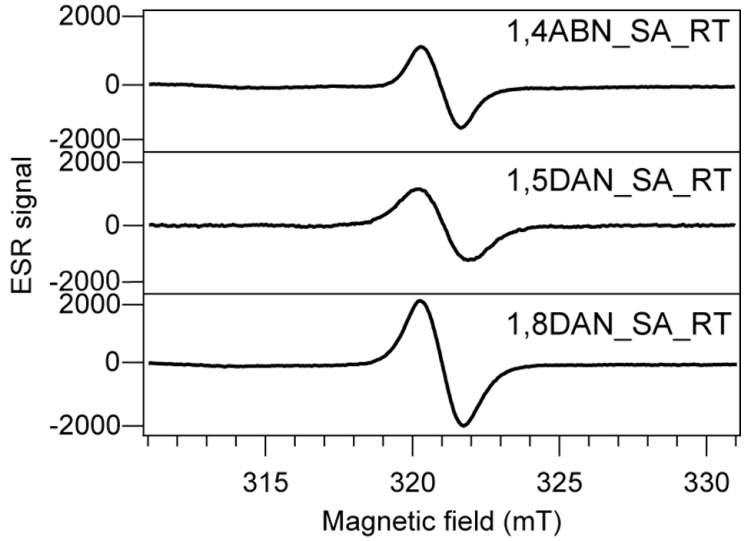

Figure S18. X-band ESR spectra of 1A4BN_SA, 15DAN_SA, and 18DAN_SA.

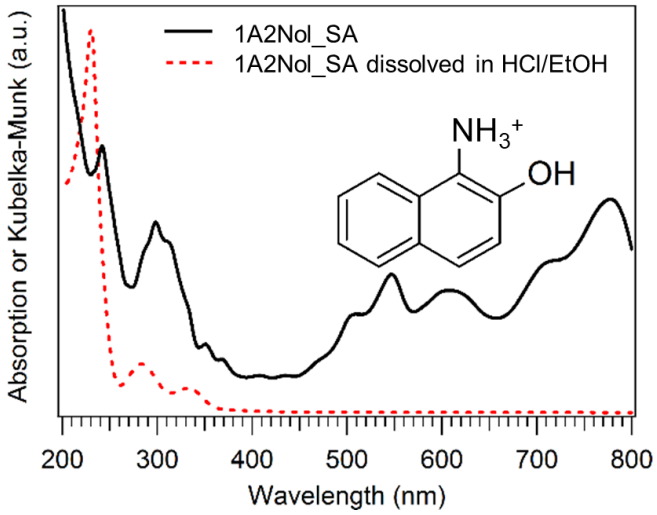

Figure S19. Transmittance absorption spectrum of 1 mM 1-ammonium-2-naphthol (1A2Nol) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 1A2Nol (solid). Reaction conditions: SA (1 g), 1A2Nol (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

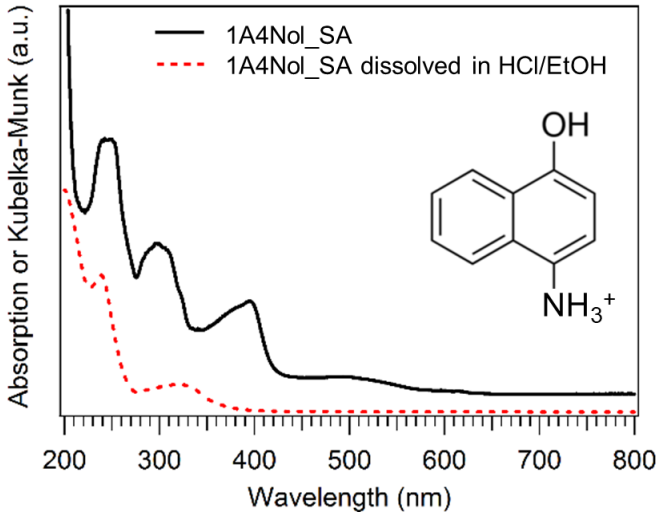

Figure S20. Transmittance absorption spectrum of 1 mM 1-ammonium-4-naphthol (1A4Nol) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 1A4Nol (solid). Reaction conditions: SA (1 g), 1A4Nol (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

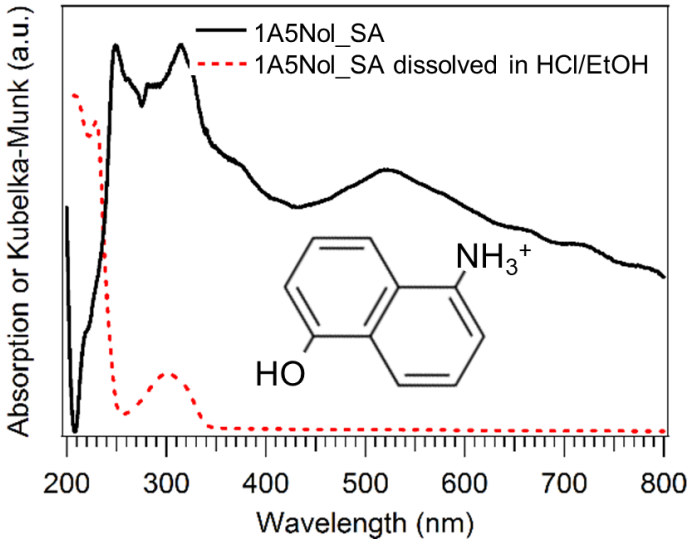

Figure S21. Transmittance absorption spectrum of 1 mM 1-ammonium-5-naphthol (1A5Nol) of 1:1 vol% 1 M HCl/EtOH (dotted) and diffuse reflectance spectrum of SA reacted with 1A5Nol (solid). Reaction conditions: SA (1 g), 1A5Nol (0.2 mmol), 1:1 vol% 1 M HCl/EtOH (200 mL) at RT, 24 h.

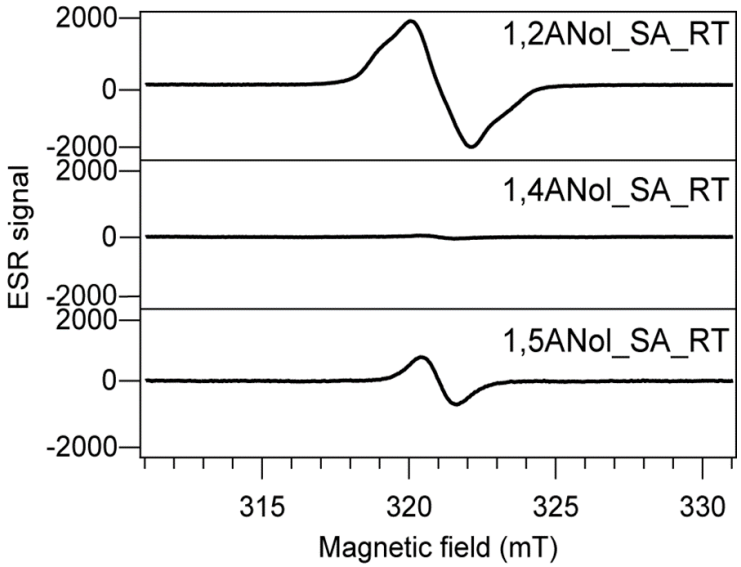

Figure S22. X-band ESR spectra of 1A2Nol_SA, 1A4Nol_SA, and 1A5Nol_SA.

Table S1. CHN results of SA reacted with naphtylammonium with various substituents.

Sample	H (wt%)	C (wt%)	N (wt%)	Measured C/N (mol/mol)	Theoretical C/N (mol/mol)
1A4BN_SA	2.37	3.02	0.090	39.1	10
15DAN_SA	2.09	2.61	0.083	36.7	5
18DAN_SA	2.22	1.71	0.119	16.8	5
1A2Nol_SA	2.55	3.27	0.078	48.9	10
1A4Nol_SA	2.28	2.13	0.146	17.0	10
1A5Nol_SA	2.62	2.55	0.042	70.8	10

6. Stability and reactivity of anthracene radical cations within SA.

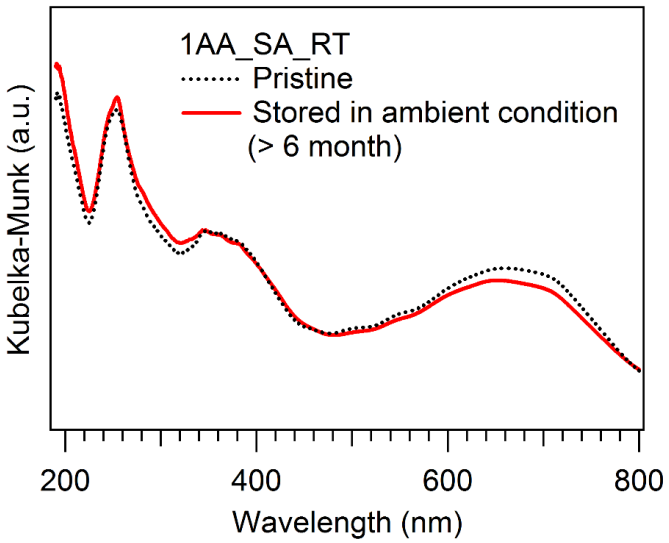

Figure S23. Diffuse reflectance spectra of 1AA_SA_RT after exposure in ambient condition over 6 months.

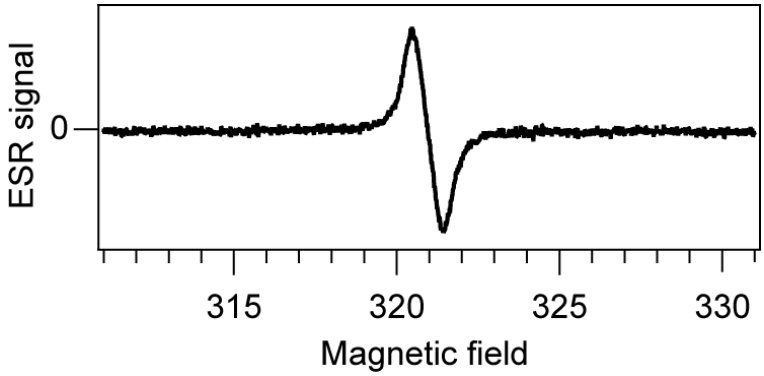

Figure S24. ESR spectra of 1AA_SA_RT after exposure in ambient condition over 6 months.

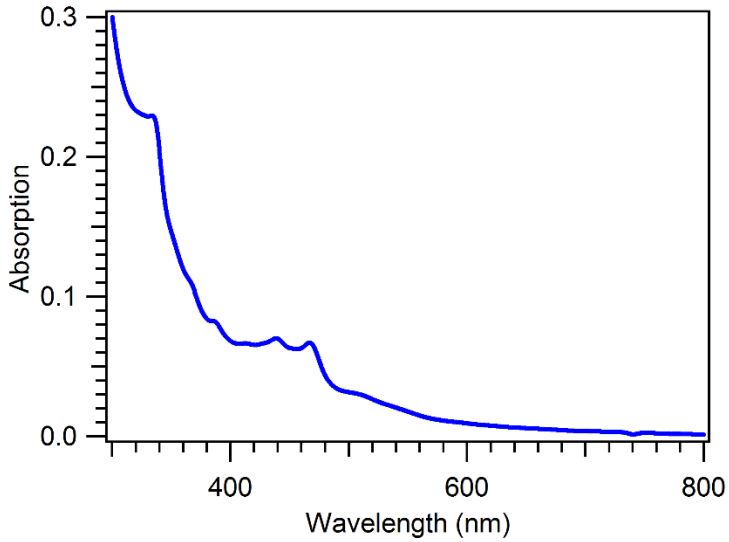

Figure S25. Absorption spectrum of the surpernatant turned yellow after the reaction of 1AA_SA_RT with AIBN

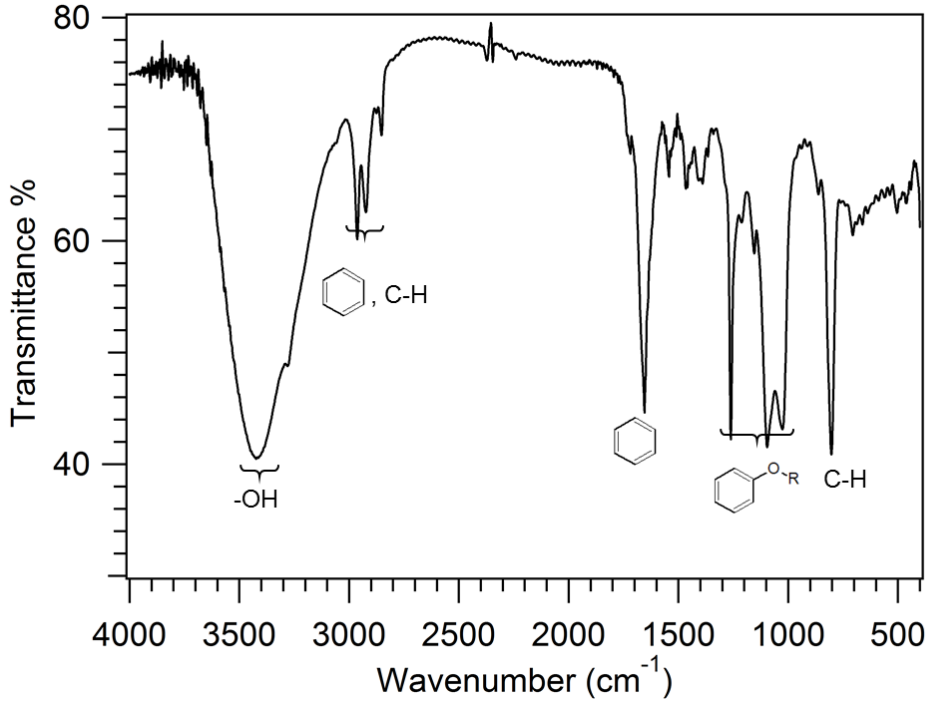

Figure S26. Absorption spectrum of the resultant of 1AA_SA_RT reacted with AIBN.