Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Mechanistic understanding of monovalent cation transport in eumelanin pigments

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Supporting Information

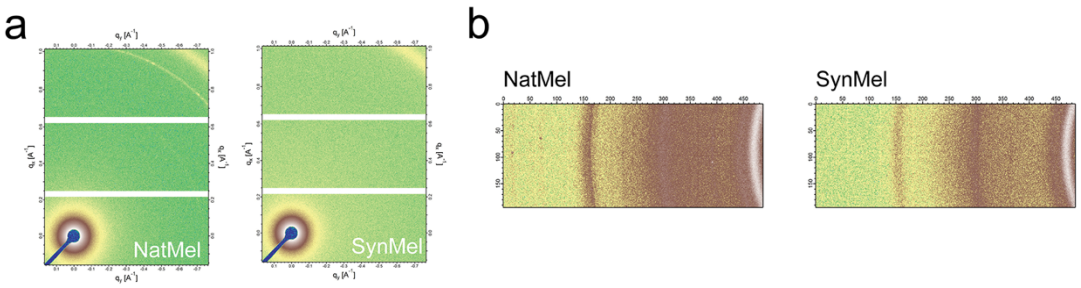

Fig. S1. Images of (a) Small-angle x-ray scattering (SAXS) and (b) wide-angle x-ray scattering (WAXS) suggest that NatMel contains the semi-crystalline structure in meso scale but SynMel shows amorphous phase.

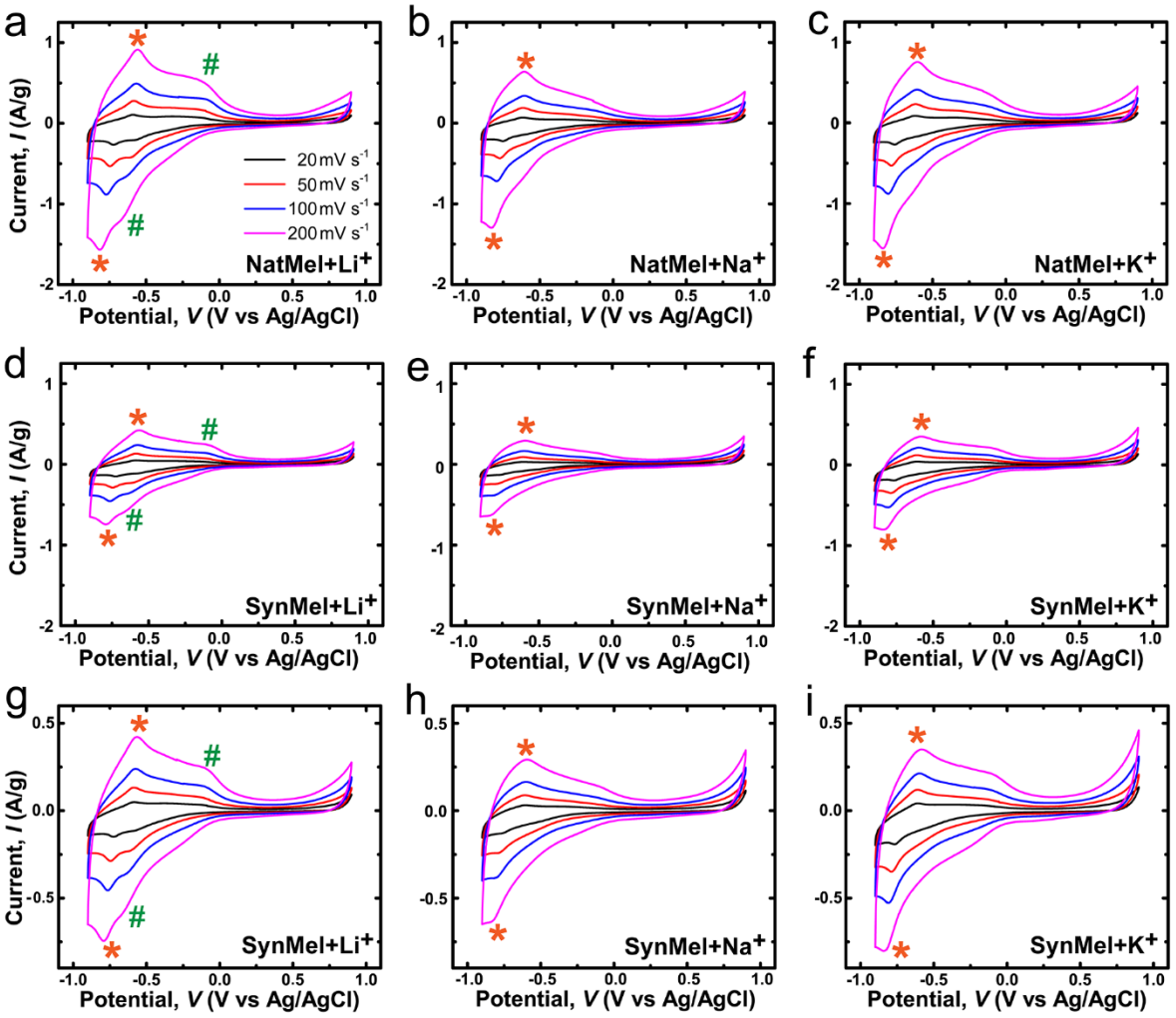

Fig. S2. Cyclic voltammetry (CV) of (a-c) NatMel and (d-i) SynMel are measured in 0.5 M Li_2SO_4, Na_2SO_4, and K_2SO_4 at the scan rates from 20 to 200 mV s^{-1}. CV of SynMel are shown in two current scales of (d-f), and (g-i) for the direct comparison with NatMel. CVs show that the monovalent cations can reversibly bind with both melanins. Cathodic/anodic peaks from CV correspond to simultaneous desertion/insertion of cations with the oxidation/reduction of melanin electrodes. The redox couples at (*) (-0.70)/(-0.58)V, and (#) (-0.54)/(-0.31)V represent the association of pendant carboxylates, and aromatic amines, respectively. The redox couple at (+) (-0.41)/(0.4)V which represent the association of catechols functional group was submerged at the scan rates from 20 to 200 mV s^{-1}.

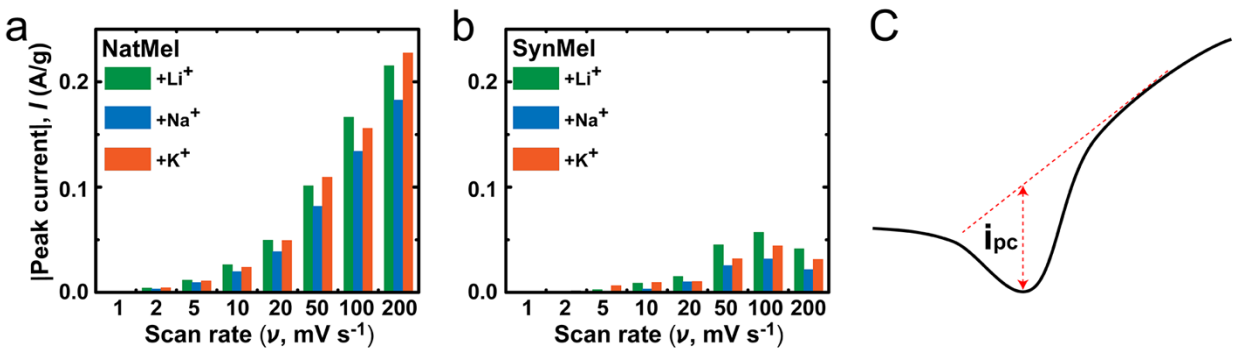

Fig. S3. The absolute values of peak current at the scan rate from 1 to 200 mV s^{-1} are shown for (a) NatMel, and (b) SynMel. (c) shows a typical approach to calculate the peak current.

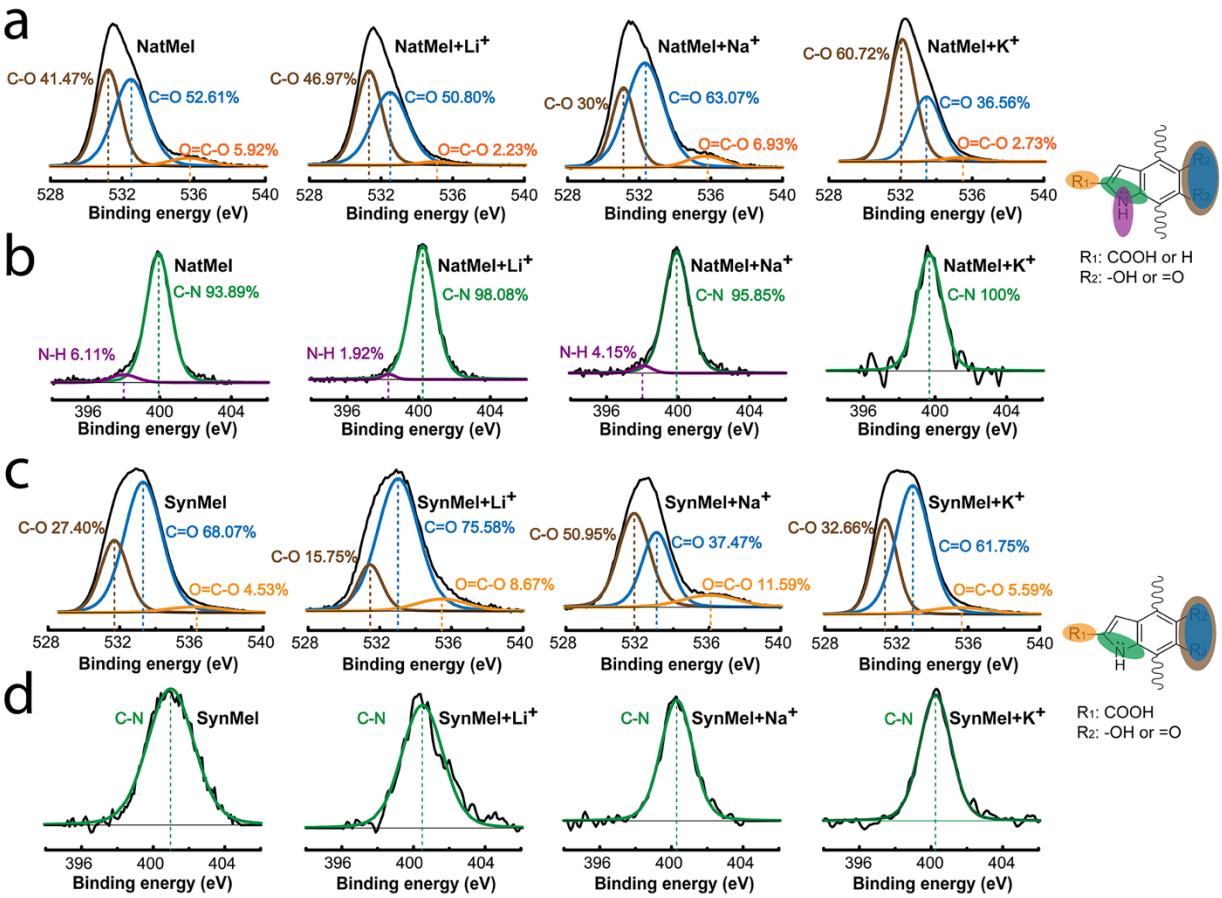

Fig. S4. High-resolution (a,c) O 1s and (b,d) N 1s XPS from pristine, and cation-associated melanins: (a) O 1s of NatMel, and (b) N 1s of NatMel; (c) O 1s of SynMel, and (d) N 1s of SynMel. Black lines represent the raw XPS spectra. Peak fitting was done by CasaXPS and shown as colored lines. Deconvoluted peaks of oxygen at the binding energies of 531.62 ± 0.49, 532.89 ± 0.57, and 535.61 ± 0.58 eV correspond to C-O, C=O, and O=C–O, respectively. Peaks from nitrogen at the binding energies of 400.34 ± 0.65, and 398.17 ± 0.17 eV correspond to the chemical functional groups of C-N, and N-H, respectively.

			a		b		R^2
			Value	Standard error	Value	Standard error	
NatMel	Anodic	Li^+	0.00733	0.00138	0.91174	0.03731	0.9968
		Na^+	0.0049	0.00087	0.91937	0.03494	0.99747
		K^+	0.00671	0.00112	0.89226	0.03304	0.99754
	Cathodic	Li^+	0.02557	0.02557	0.77516	0.01492	0.99902
		Na^+	0.0208	0.00222	0.77779	0.02134	0.998
		K^+	0.0262	0.00222	0.76921	0.01697	0.01697
SynMel	Anodic	Li^+	0.00663	0.00096	0.78533	0.00054	0.99807
		Na^+	0.00492	0.0008	0.76455	0.02464	0.99758
		K^+	0.00677	0.00108	0.74665	0.0241	0.99748
	Cathodic	Li^+	0.01411	0.00139	0.75661	0.01664	0.99856
		Na^+	0.01671	0.00103	0.68549	0.01245	0.99915
		K^+	0.03327	0.00176	0.60022	0.01085	0.999

Table S1. Fitting parameters used to fit the data according to the equation: $i = av^b$ (Fig. 3) for both the NatMel and SynMel with Li^+, Na^+, and K^+.