Supporting Information for

Using Solid-State NMR to Monitor the Molecular Consequences of *Cryptococcus neoformans* Melanization with Different Catecholamine Precursors

Subhasish Chatterjee,[†] Rafael Prados-Rosales,[‡] Susana Frases,[‡,⊥] Boris Itin,[§] Arturo Casadevall,[‡] and Ruth E. Stark*,[†]

[†]Department of Chemistry, City College of New York, Graduate Center and Institute for Macromolecular Assemblies, City University of New York, New York, New York 10031, United States

[‡]Department of Microbiology and Immunology, Albert Einstein College of Medicine, Yeshiva University, Bronx, New York 10461, United States

[§]New York Structural Biology Center, New York, New York 10027, United States

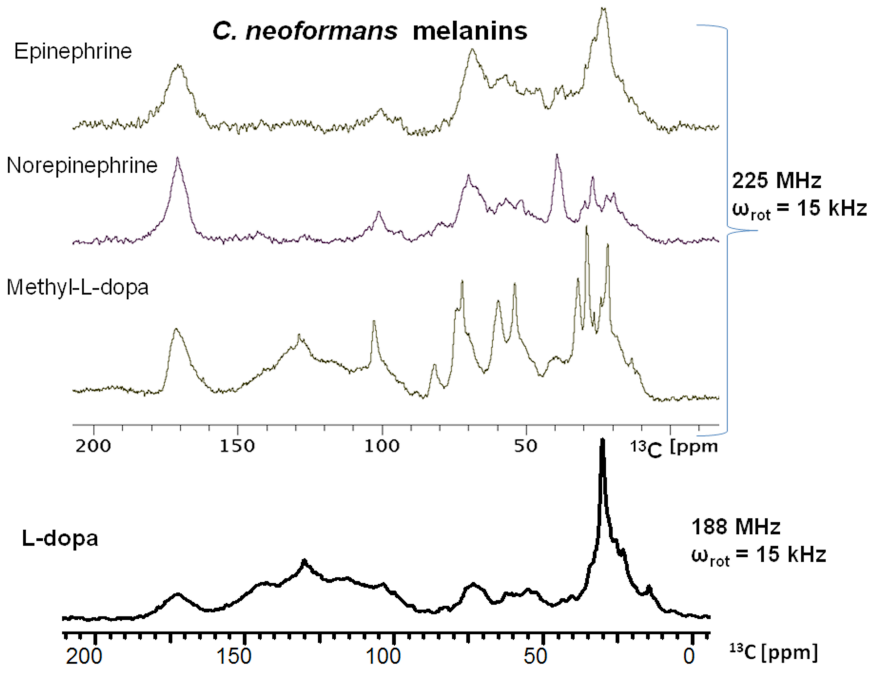

Figure S1. 188 and 225 MHz CPMAS solid-state ^{13}C NMR spectra of *C. neoformans* melanins obtained by *in vitro* biosynthesis, showing enhanced resolution as compared with analogous spectra at a ^{13}C frequency of 150 MHz (Figure 1). Comparisons of the L-dopa and epinephrine melanin spectra in Figures 1 and S1, which are derived from separate fungal preparations, also attest to the reproducibility of the growth and extraction procedures.

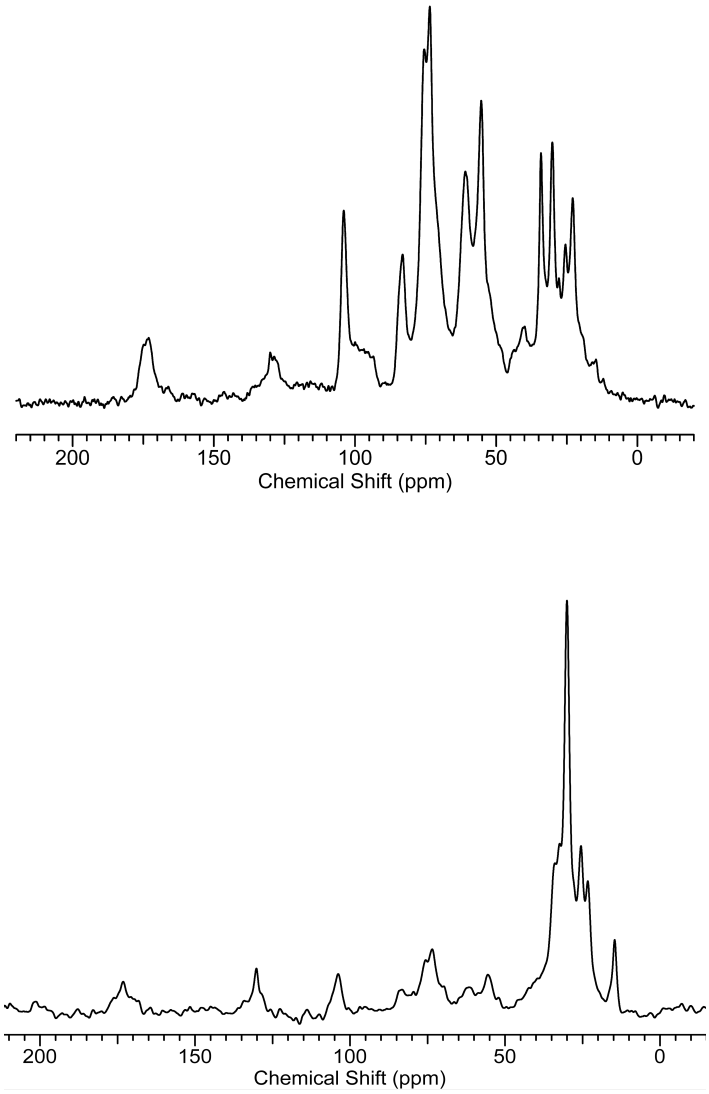

Figure S2. (Top) 150 MHz ^{13}C CPMAS Spectrum of *C. neoformans* melanin produced with norepinephrine and U-^{13}C-glucose. The spectrum was acquired at 15 kHz spinning frequency. (Bottom) 150 MHz ^{13}C CPMAS Spectrum of *C. neoformans* melanin produced with epinephrine and U-^{13}C-glucose. The spectrum was acquired at 10 kHz spinning frequency.

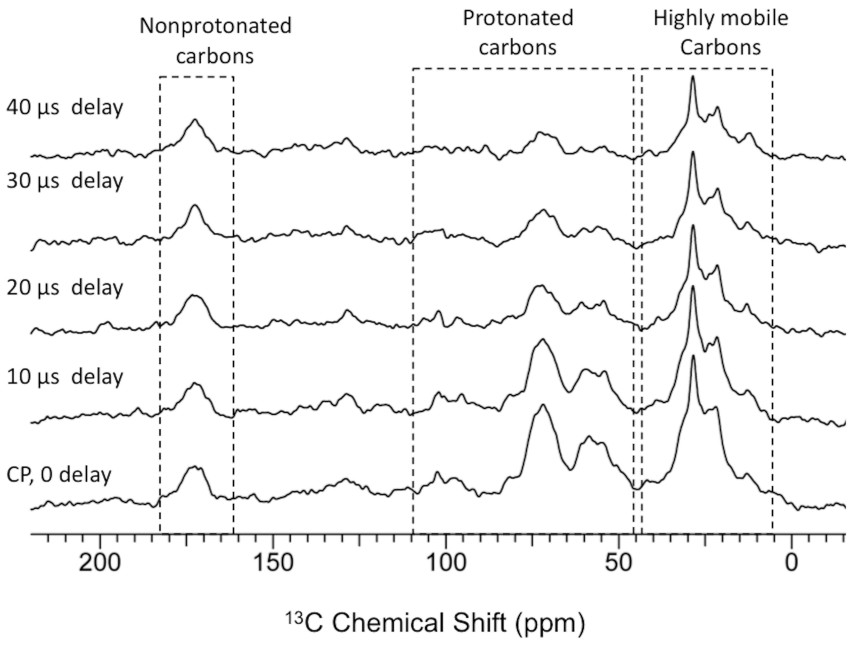

Figure S3. 150 MHz CPMAS solid-state ^{13}C spectra of *C. neoformans* melanin produced with natural abundance L-dopa and [U-$^{13}C_6$]-glucose. All data were acquired at a 10 kHz spinning frequency and with delayed decoupling, the introduction of a series of time delays (10-40 µs) in the proton decoupling which permitted the dephasing of NMR signals from rigid singly and doubly protonated carbons.

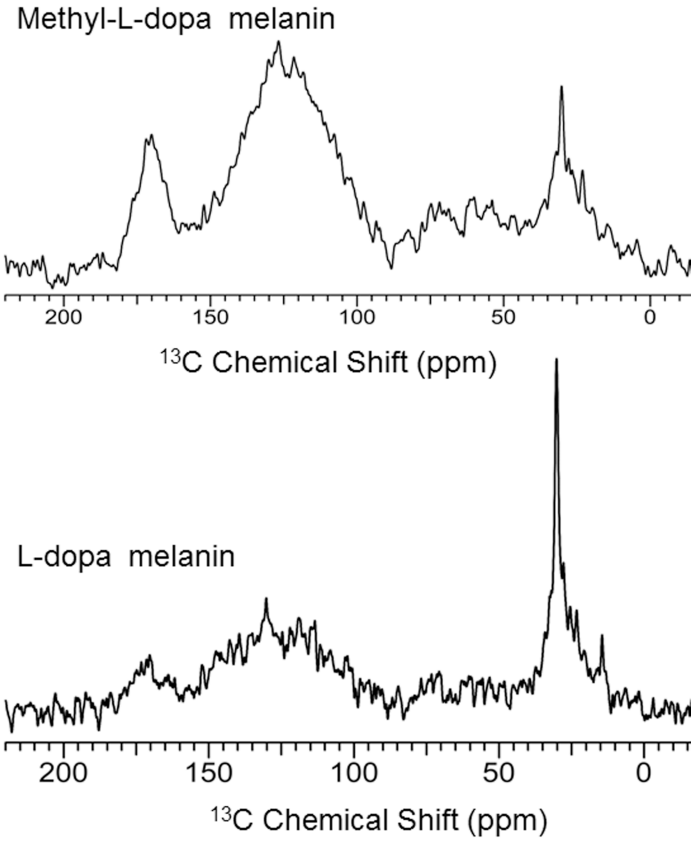

Figure S4. 150 MHz ^{13}C DPMAS spectra of *C. neoformans* melanins produced with L-dopa and methyl-L-dopa. All spectra were acquired at a 15 kHz spinning speed.

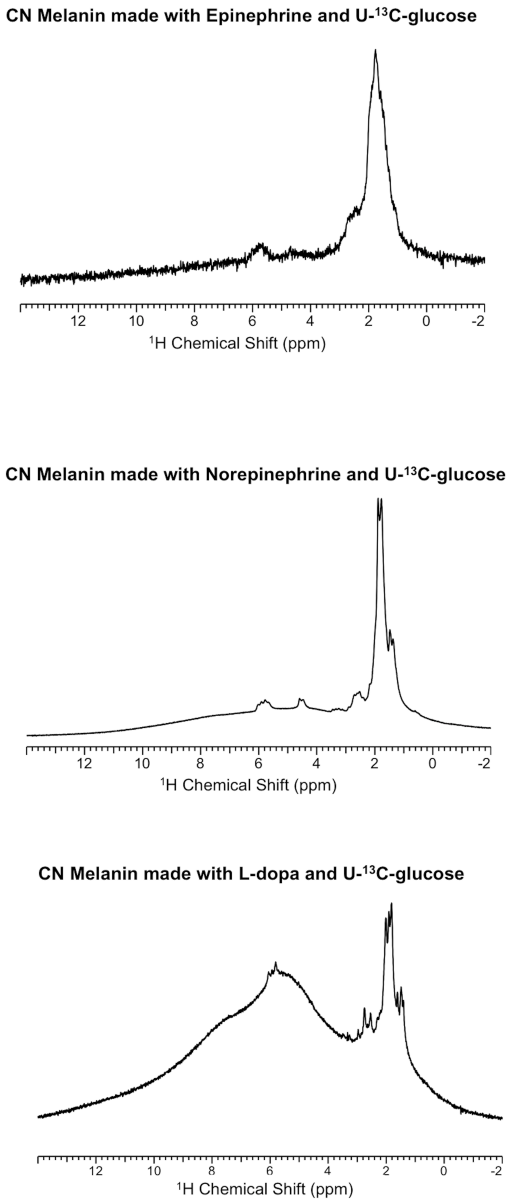

Figure S5. Solid-state MAS ^{1}H spectra of *C. neoformans* (CN) melanins produced from U-^{13}C-glucose and natural abundance L-dopa, norepinephrine, and epinephrine acquired at a ^{1}H frequency of 600 MHz. A spinning rate of 35 kHz was used to acquire all spectra except for epinephrine, which was obtained at 15 kHz; chemical shifts were referenced indirectly, using a calculation from gyromagnetic ratios of ^{1}H and ^{13}C according to IUPAC recommendations. [1]

Reference Cited

(1) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Solid State Nucl Mag* **2002**, *22*, 458.