

Solid-State [2+2] Photoreaction of Isostructural Cd(II) Metal Complexes and Solid-State Fluorescence

Akansha Ekka ¹, Aditya Choudhury ¹, Madhumita Samanta ¹, Ayushi Deshmukh ¹, Nathan R. Halcovitch ², In-Hyeok Park ^{3,*} and Raghavender Medishetty ^{1,*}

¹ Department of Chemistry, Indian Institute of Technology Bhilai, Kutelabhata, Durg 491001, India

² Chemistry Department, Lancaster University, LA1 4YB, United Kingdom

³ Graduate School of Analytical Science and Technology (GRAST), Chungnam National University, Daejeon 34134, Republic of Korea

* Correspondence: ipark@cnu.ac.kr (I.-H.P.); raghavender@iitbhilai.ac.in (R.M.)

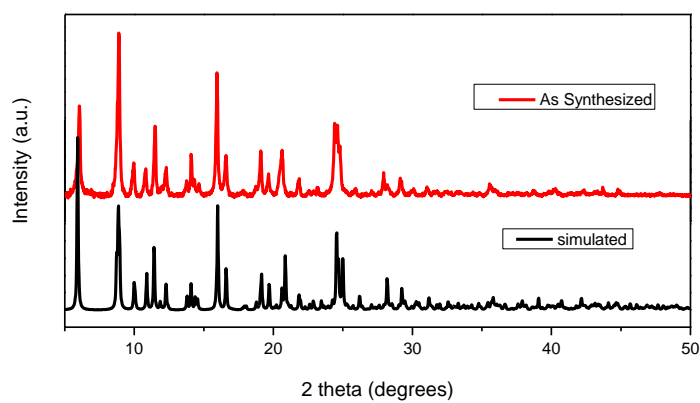


Figure S1. Comparison of SCXRD simulated & experimental PXRD pattern of 1.

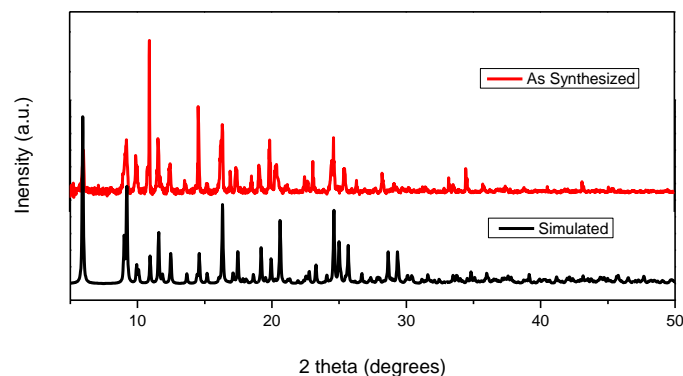


Figure S2. Comparison of SCXRD simulated & experimental PXRD pattern of 2.

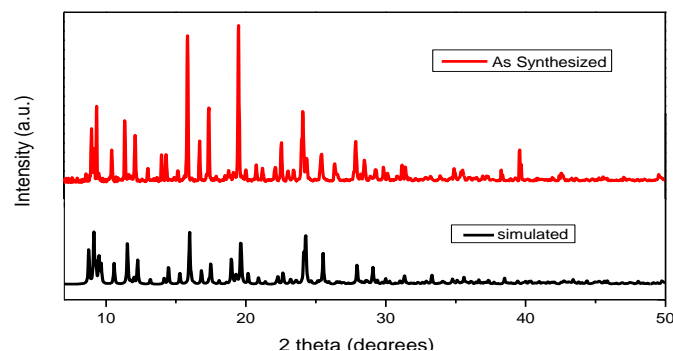


Figure S3. Comparison of SCXRD simulated & experimental PXRD pattern of 3.

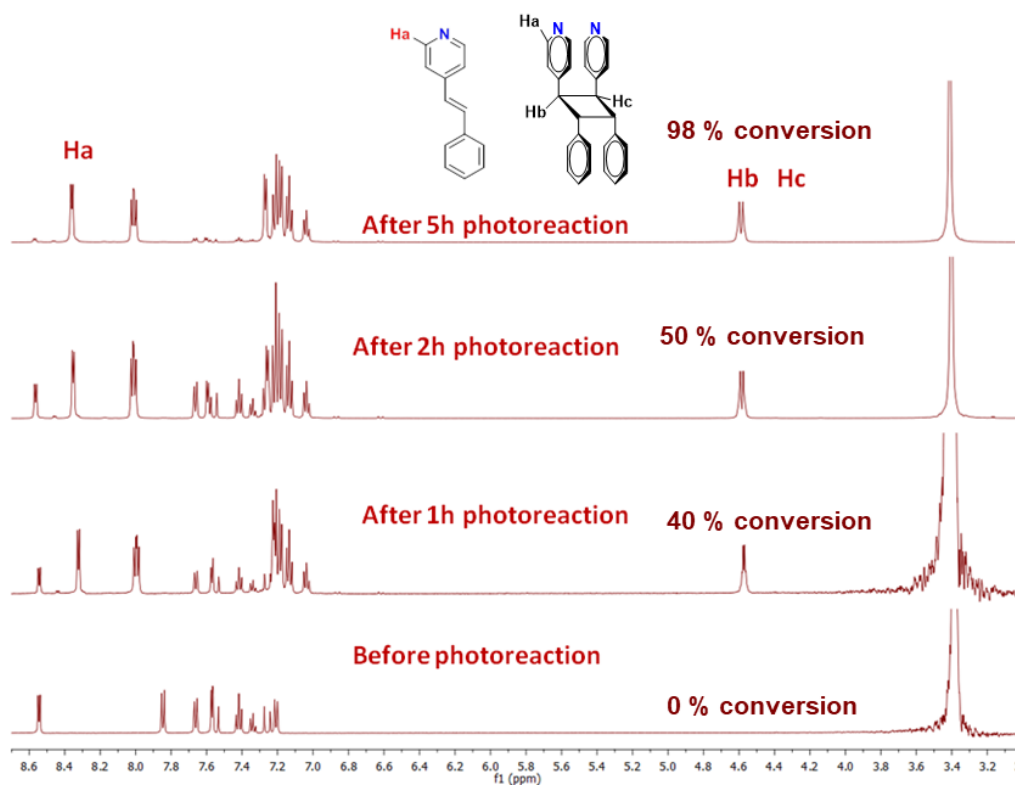


Figure S4. Time-dependent ^1H NMR plot of **2**.

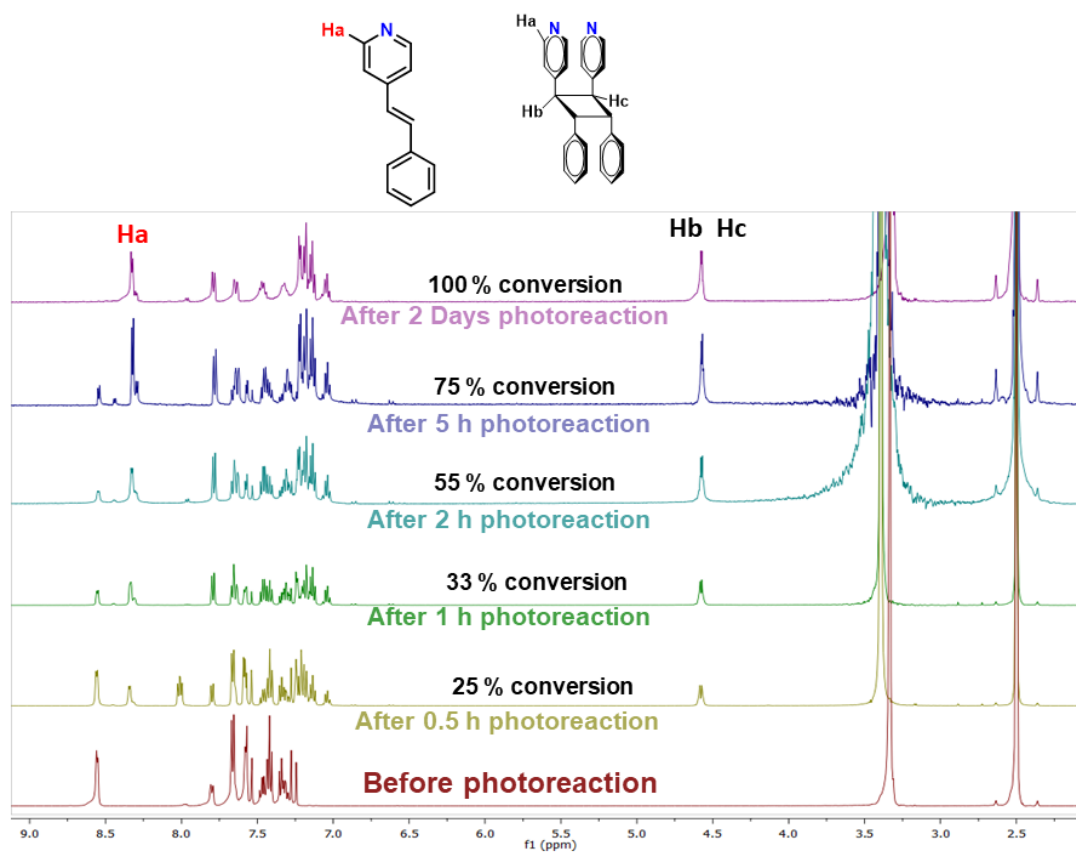


Figure S5. Time-dependent ^1H NMR plot of **3**.

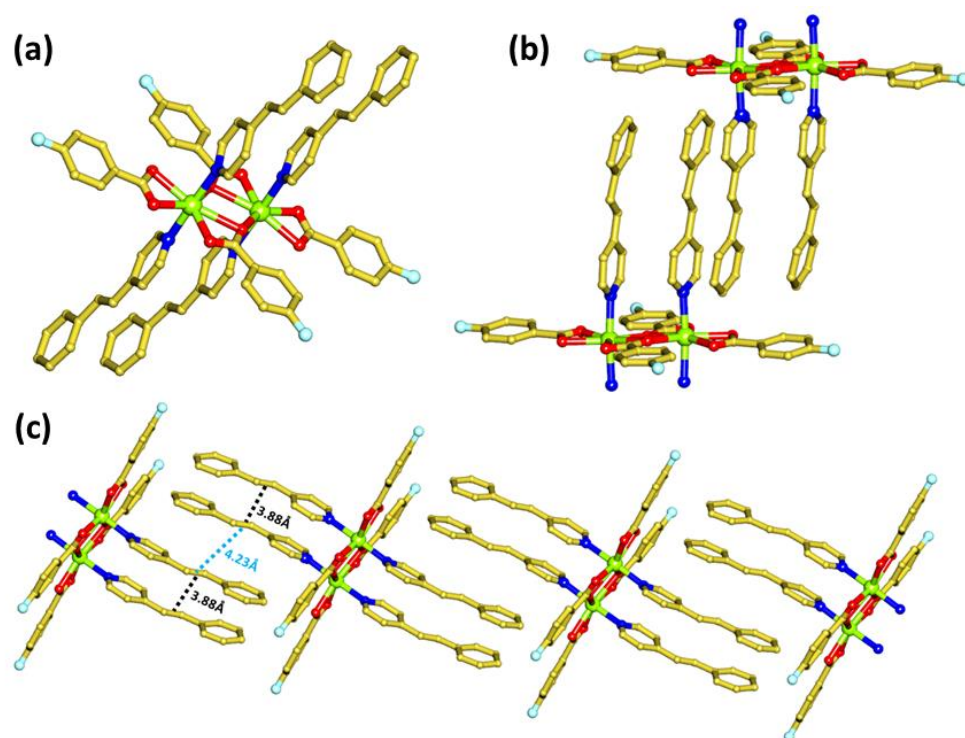


Figure S6. Crystal structure of $[\text{Cd}_2(4\text{FBA})_4(4\text{spy})_4]$ (2). (a) Metal complex of 2. (b) Alignment of the photoreactive linker in 2. (c) Extended head-to-head and head-to-tail alignment. All H-atoms are omitted for clarity. Colour codes: C = golden; N = dark blue; O = red; F= cyan; Cd = green.

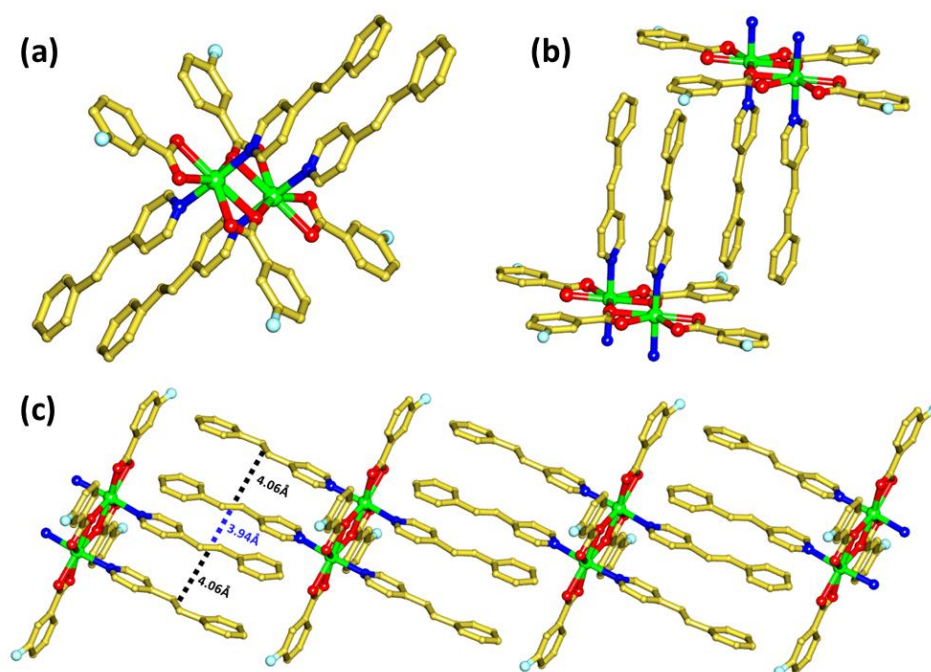


Figure S7. Crystal structure of $[\text{Cd}_2(3\text{FBA})_4(4\text{spy})_4]$ (3). (a) Metal complex of 3. (b) Alignment of the photoreactive linker in 3. (c) Extended head-to-head and head-to-tail alignment. All H-atoms are omitted for clarity. Colour codes: C = golden; N = dark blue; O = red; F= cyan; Cd = green.

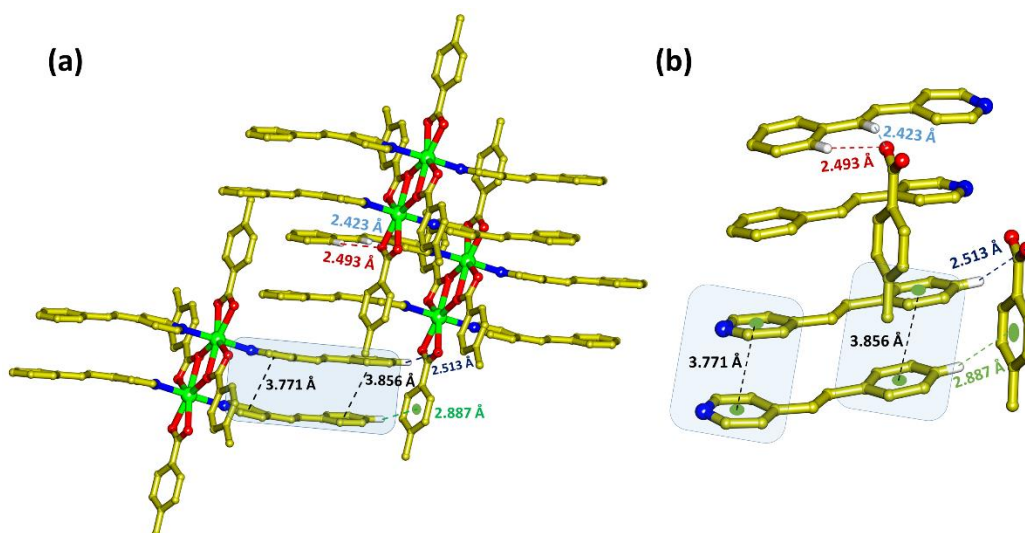


Figure S8. Depiction of non-covalent interactions in $[\text{Cd}_2(\text{p-tol})_4(4\text{spy})_4]$ (1). (a) π - π interactions are shown as blue shade. C-H... π interactions are shown as green dashed line. C-H...O interactions are shown as blue (dark and light) and red dashed line. (b) Enlarged view of photoreactive linker depicting non-covalent interactions. All H-atoms are omitted for clarity. Colour codes: C = golden; N = dark blue; O = red; Cd = green.

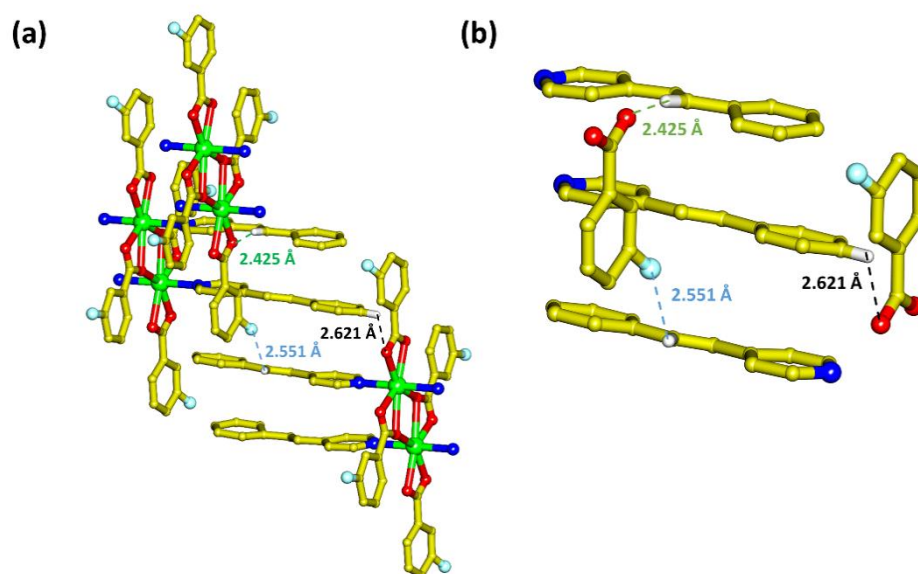


Figure S9. Depiction of non-covalent interactions in $[\text{Cd}_2(3\text{FBA})_4(4\text{spy})_4]$ (3). (a) C-H...F interactions are shown as blue dashed line. C-H...O interactions are shown as black and green dashed line. (b) Enlarged view of photoreactive linker depicting non-covalent interactions. All H-atoms are omitted for clarity. Colour codes: C = golden; N = dark blue; O = red; F = cyan; Cd = green.

Table S1. Bond lengths along the coordination geometry of Cd(II) ion.

Compound-1:

Bond between	Length (Å)
Cd1-O1	2.4234(17)
Cd1-O2	2.3566(16)
Cd1-O3	2.3358(17)
Cd1-O4	2.5125(17)
Cd1-O4	2.3614(16)
Cd1-N1	2.325(2)
Cd1-N2	2.316(2)

Compound-2:

Bond between	Length (Å)
Cd1-O1	2.3181(15)
Cd1-O2	2.5894(15)
Cd1-O2	2.3317(14)
Cd1-O3	2.3832(14)
Cd1-O4	2.4033(15)
Cd1-N1	2.3072(18)
Cd1-N2	2.296(6)

Compound-3:

Bond between	Length (Å)
Cd1-O1	2.352(3)
Cd1-O2	2.378(2)
Cd1-O2	2.529(3)
Cd1-O3	2.404(3)
Cd1-O4	2.379(3)
Cd1-N1	2.320(3)
Cd1-N2	2.327(3)

Compound-4r:

Bond between	Length (Å)
Cd1-O1	2.426(7)
Cd1-O2	2.389(9)
Cd1-O3	2.373(9)
Cd1-O4	2.469(12)
Cd1-O5	2.352(7)
Cd1-N1	2.329(8)
Cd1-N2	2.355(8)
Cd2-O6	2.311(10)
Cd2-O7	2.631(14)
Cd2-O8	2.407(8)
Cd2-O9	2.398(10)
Cd2-O10	2.340(7)
Cd2-N3	2.324(9)
Cd2-N4	2.326(8)