Two act as one: unexpected dimers of catechol direct a solid-state [2+2] photodimerization in a six-component hydrogen-bonded assembly

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Supplemental Information

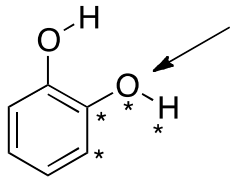
Reagents

Catechol and nitromethane were purchased from Acros Organics. 1,2-bis(2-pyridyl)ethylene was purchased from Sigma-Aldrich. Acetonitrile was purchased from Fisher Scientific. All chemicals were used as received and without further purification.

Experimental

Solid-state photodimerizations: UV-irradiation experiments were performed by placing single crystals of **1** on a watch glass or finely-ground samples of **1** between two pyrex plates and regularly turning the samples to ensure uniform irradiation.

Reported angles for *gauche* hydroxyl groups of **cat** in *syn-gauche* conformation were measured as the dihedral angle defined in scheme below. When viewed along the O-C bond, a clockwise rotation of the O-H group was defined to have a positive value.



Scheme S1. Measured dihedral angle of *syn-gauche* catechols.

2) Single-Crystal X-ray diffraction Measurements

Single-crystal XRD data were collected on a Nonius Kappa CCD single-crystal X-ray diffractometer using MoK_α radiation (λ = 0.71073 Å). Using Olex2,[1] structure solution and refinement were accomplished using SHELXS-97 and SHELXL-97, respectively.[2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained positions.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{24}H_{22}N_2O_4$
Formula weight	402.43
Temperature/K	190.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.3687(7)
b/Å	19.169(2)
c/Å	14.7014(15)
α/°	90
β/°	102.277(5)
γ/°	90
Volume/Å^3	2029.1(4)
Z	4
ρ_{calc}g/cm^3	1.317
μ/mm^{-1}	0.090
Crystal size/mm^3	0.38 × 0.1 × 0.1
Radiation	MoKα (λ = 0.7107)
Reflections collected	16490
Independent reflections	4648 [R_{int} = 0.0357, R_{sigma} = 0.0370]
Goodness-of-fit on F^2	1.099
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1164
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.1485
CCDC Deposition Number	1025307

Table S2. Crystal data and structure refinement for **1** (SCSC).

Empirical formula	$C_{24}H_{22}N_2O_4$
Formula weight	402.43
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4665(8)
b/Å	19.1328(19)
c/Å	14.8336(15)
α/°	90
β/°	102.249(5)
γ/°	90
Volume/Å^3	2070.8(4)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.089
Crystal size/mm^3	0.3 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
Reflections collected	10870
Independent reflections	3631 [R_{int} = 0.0324, R_{sigma} = 0.0301]
Goodness-of-fit on F^2	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0589, wR_2 = 0.1442
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.1548
CCDC Deposition Number	1025308

Table S3. Crystal data and structure refinement for **2**.

Empirical formula	$C_{42}H_{38}N_4O_6$
Formula weight	694.76
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	11.9841(12)
b/Å	12.6106(13)
c/Å	13.7902(14)
α/°	109.918(5)
β/°	103.137(5)
γ/°	102.958(5)
Volume/Å^3	1801.6(3)
Z	2
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	0.087
Crystal size/mm^3	0.33 × 0.3 × 0.12
Radiation	MoKα (λ = 0.71073)
Reflections collected	9665
Independent reflections	5711 [R_{int} = 0.0192, R_{sigma} = 0.0337]
Goodness-of-fit on F^2	1.139
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1451
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1776
CCDC Deposition Number	1025309

3) Powder X-ray Diffraction

Powder X-ray diffraction data were collected from samples mounted on glass slides using a Siemens D5000 X-ray diffractometer using $CuK_{\alpha 1}$ radiation (λ = 1.54056 Å) (scan type: locked coupled; scan mode: continuous; step size: 0.02°).

Figure S1. Experimental X-ray powder pattern of **1** (before reaction).

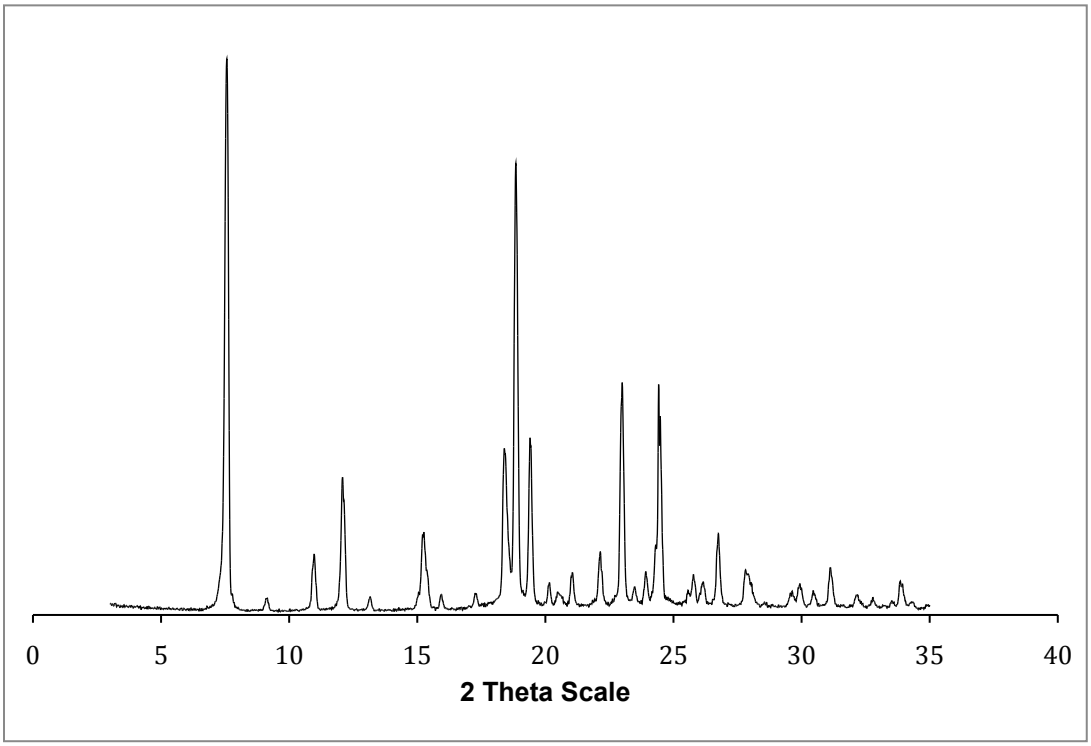
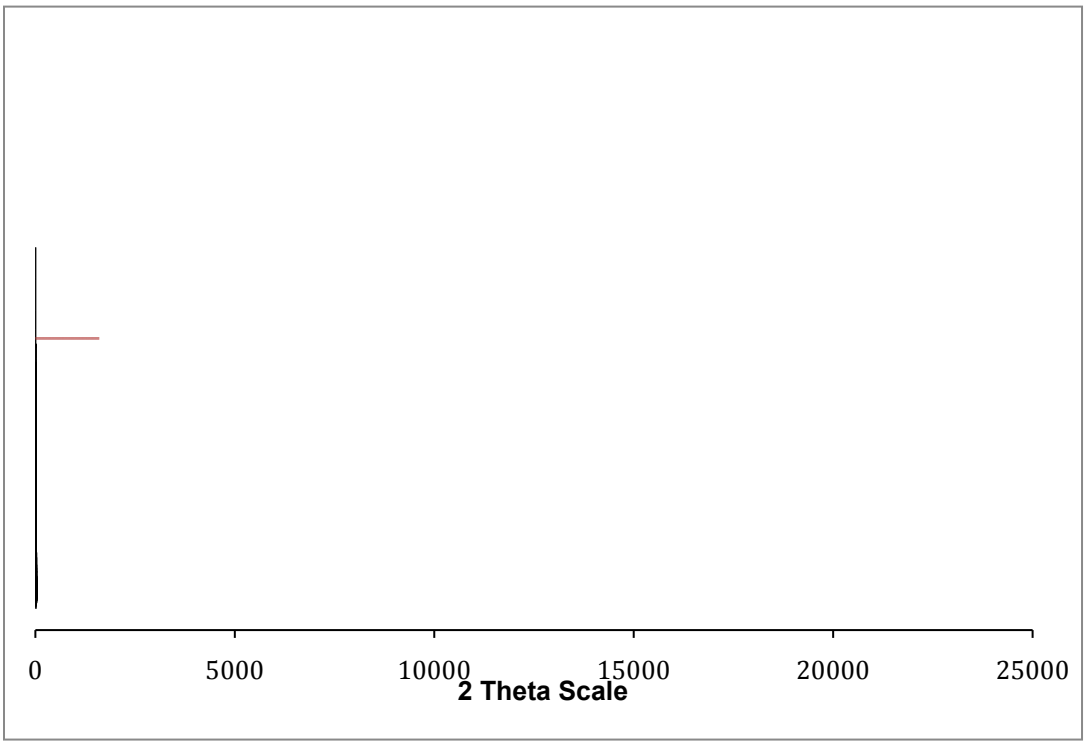


Figure S2. Experimental X-ray powder pattern of **1** (after reaction).



4) ^{1}H NMR spectroscopy

^{1}H NMR data were collected on an AVANCE Bruker NMR spectrometer operating at 300 MHz using DMSO-d_6 as the solvent.

Figure S3. ^{1}H NMR spectrum of **1** (prior to reaction).

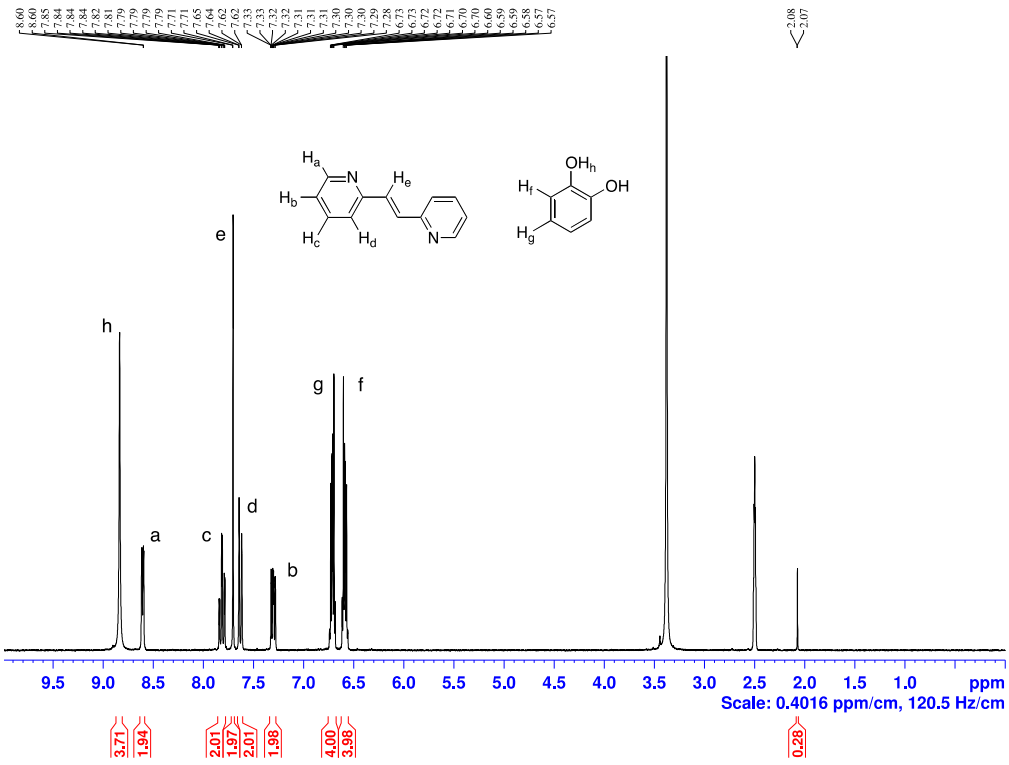


Figure S4. ^{1}H NMR spectrum of **1** (following exposure to broadband Hg lamp).

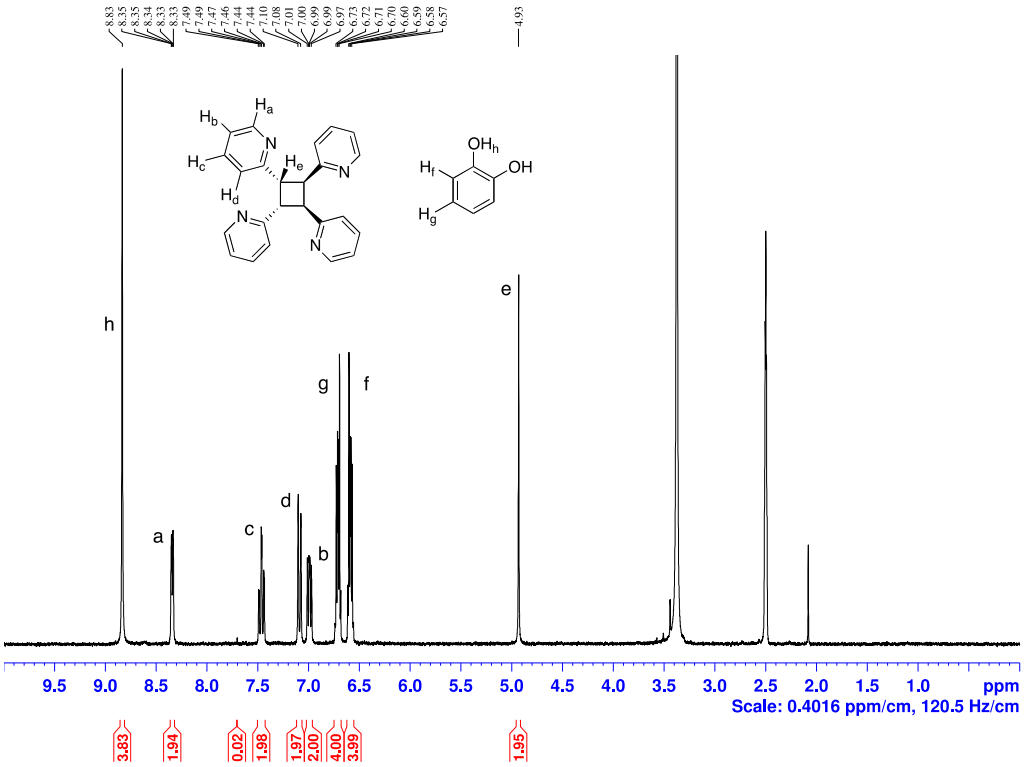


Figure S5. ^{1}H NMR spectrum of **1** (following exposure of single crystals to curing lamp).

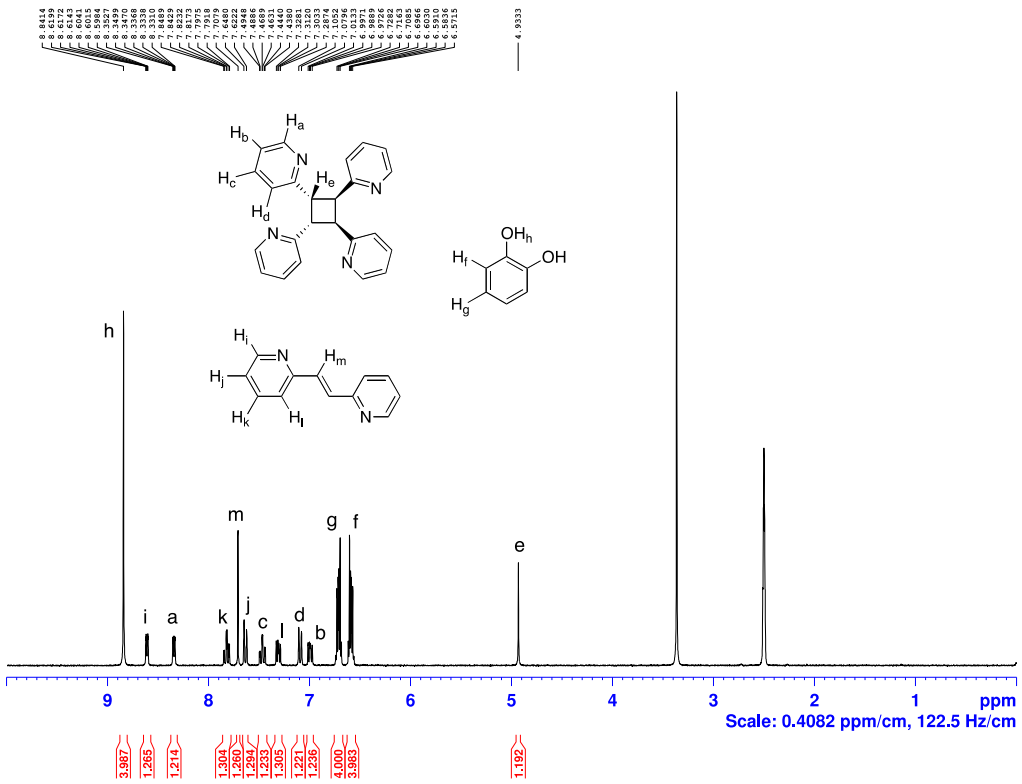
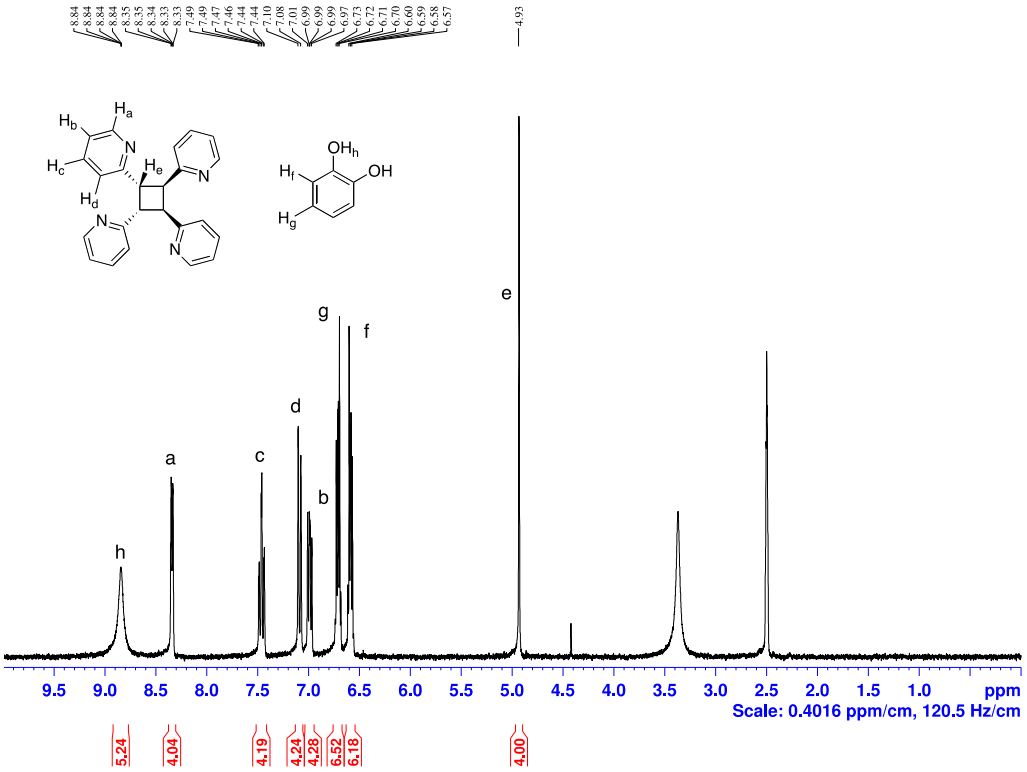


Figure S6. ^{1}H NMR spectrum of **2**.



References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

2. G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112.