

Solid-state photochemical [2+2] cycloaddition reactions involving *trans*-1,2-bis(4-pyridyl)ethylene

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Supporting information



Before UV: Yield: 113mg : (KBr, cm⁻¹): ν = 1681-1601, 1557, 1483, 1435, 1384, 1204, 1176, 1131, 972; 836; ¹H NMR (*d*₆-DMSO, 300 MHz, 298K) δ = 8.62 (d, 4H, Py-H), 7.64-7.62(m, 4H, Ph-H, 4H, Py-H), 7.60 (m, 14, Ph-H, CH=CH), 7.41-7.20(m, 16H, Ph-H), 3.83-3.79 (m, 2H, CH₂). ³¹P NMR (*d*₆-DMSO, 100 MHz, 298K): δ = 25.26 ¹³C NMR (*d*₆-DMSO, 300 MHz, 298K) :δ = 159.62(m, C-CF₃COO), 150.79(C-Py), 144(C-Py), 133-132(C-Ph), 129-128(C-Ph), 121(C- Py), 24(C-CH₂); Elemental analysis (%) calcd. for C₄₁H₃₂N₂O₄F₆P₂Ag₂: C, 48.84; H, 3.20, N, 2.78; Found: C, 49.32; H, 3.17; N, 2.53%; TG/DTA: Stable upto 220° C.

After UV irradiation of 7: [Ag₄(O₂CCF₃)₄(μ-dppm)₂ (μ-*rcit-tpcb*)_n] (100%): IR :(KBr, cm⁻¹): ν = 1668-1606; 1483; 1436; 1384; 1201-1129; 999; 831. ¹H NMR (*d*₆-DMSO, 300 MHz, 298K) : δ = 8.31 (d, 4H, Py-H), 7.61-7.59(m, 4H, Ph-H, 6H, Py-H), 7.32-7.14 (m, 14, Ph-H), 4.65(s, 2H, cbt), 3.84-3.72 (m, 2H, CH₂); ³¹P NMR (*d*₆-DMSO, 100 MHz, 298K): δ = 24.43; ¹³C NMR (*d*₆-DMSO, 300 MHz, 298K): δ = 159.32(m, C-CF₃COO), 149.91(C-Py), 148.72(C-Py), 133-128(C-Ph), 123(C-Py), 44.72(C-CH₂-CH₂), 24.15(C-CH₂). Elemental analysis (%) calcd. for C₄₁H₃₂N₂O₄F₆P₂Ag₂: C, 48.84; H, 3.20, N, 2.78; Found: C, 49.93; H, 3.91; N, 2.53%.

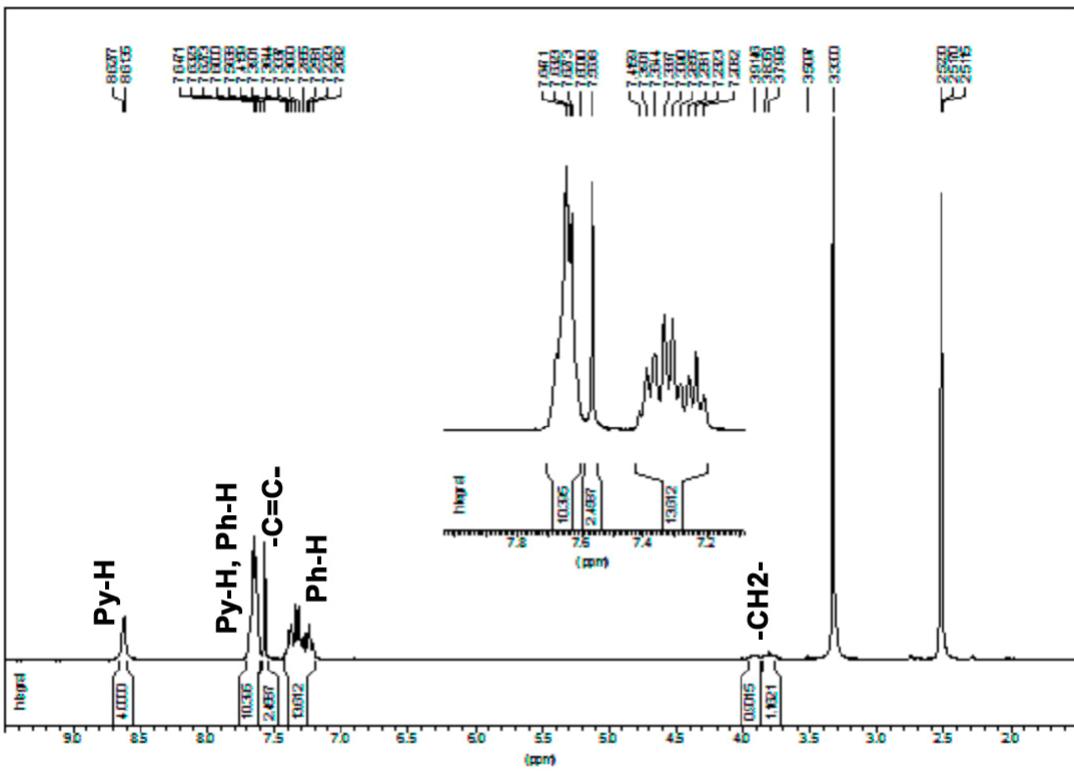


Fig. S1 ¹H NMR spectrum of 7 before UV irradiation

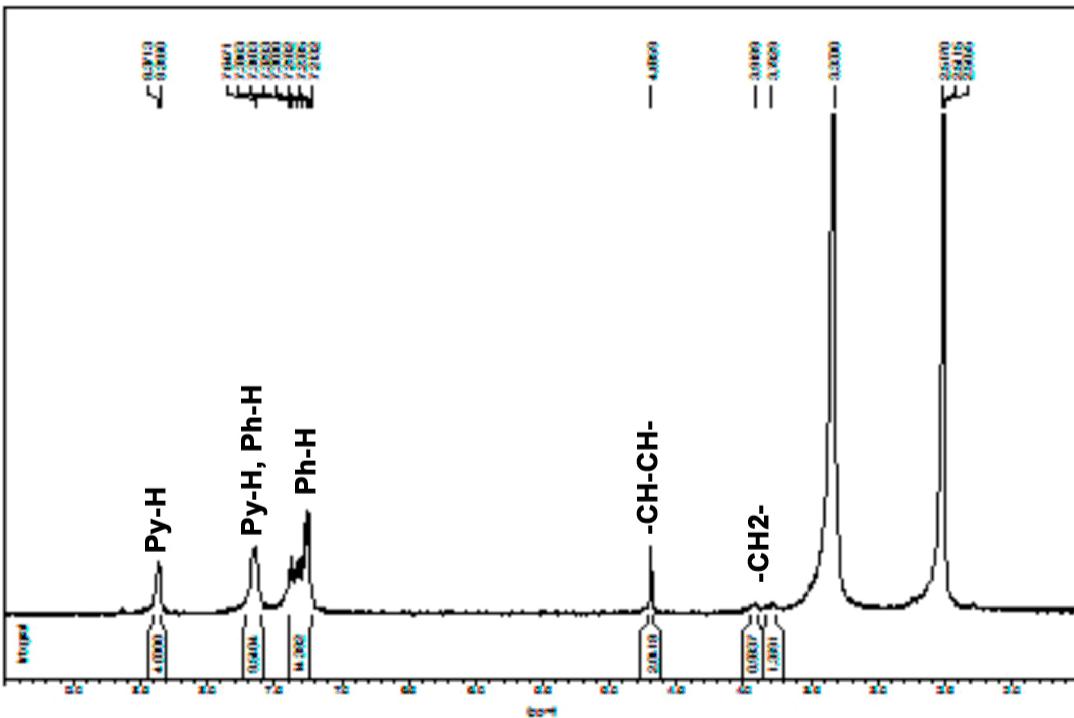


Fig. S2 ¹H NMR spectrum of 7 after UV irradiation

[Au₄(μ-dppe)₂(μ-bpe)₂](O₂CCF₃)₄, 8: Yield: 0.180 g, (20 %); ¹H NMR (*d*₆-DMSO, 300 MHz, 298K): δ = 8.57 (d, 4H, Py-H), 7.63 (m, 12H, Ar-H, Py-H), 7.54 (s, 2H, CH=CH), 7.34-7.24 (m, 12H, Ar-H,); ³¹P NMR (*d*₆-DMSO, 100 MHz, 298K): δ = 25.26; ¹H NMR (*d*₄-CH₃OH, 300 MHz, 298K): δ = 8.62 (d, 4H, Py-H), 7.90 (m, 8H, Ph-H), 7.81 (d, 4H, Py-H), 7.61 (m, 14, Ph-H, CH=CH), 3.22 (d, 4H, CH₂). Elemental analysis (%) calcd. for C₄₂H₃₀N₂O₄F₆P₂Au₂: C, 42.16; H, 2.53; N, 2.34; Found: C, 41.90; H, 2.34; N, 2.56.

After UV irradiation of [Au₄(μ-dppe)₂(μ-bpe)₂](O₂CCF₃)₄, 8 :

Photodimerization in solid state: ¹H NMR (*d*₆-DMSO, 300 MHz, 298K): δ = 8.53 (b, 4H, Py-H), 7.75 (b, 12H, Ar-H, Py-H), 7.51-7.25 (m, 12H, Ar-H), 4.92 (s, 2H, CH-CH). ³¹P NMR (*d*₆-DMSO, 100 MHz, 298K): δ = 24.46; ¹H NMR (*d*₄-CH₃OH, 300 MHz, 298K): δ = 8.60 (d, 4H, Py-H), 7.91 (m, 8H, Ar-H), 7.88 (d, 4H, Py-H), 7.62-7.59 (m, 12H, Ar-H), 4.62 (s, 2H, CH-CH), 3.22 (d, 4H, CH₂); Elemental analysis (%) calcd. for C₄₂H₃₀N₂O₄F₆P₂Au₂: C, 42.16; H, 2.53; N, 2.34; Found: C, 41.75; H, 2.30; N, 2.32.

Photodimerization in solution: ¹H NMR (*d*₆-DMSO, 300 MHz, 298K): δ = 8.53 (d, 4H, Py-H), 7.79-7.41 (m, 24H, Py-H, Ar-H), 4.92 (s, 2H, CH-CH). ³¹P NMR (*d*₆-DMSO, 100 MHz, 298K): δ = 25.00

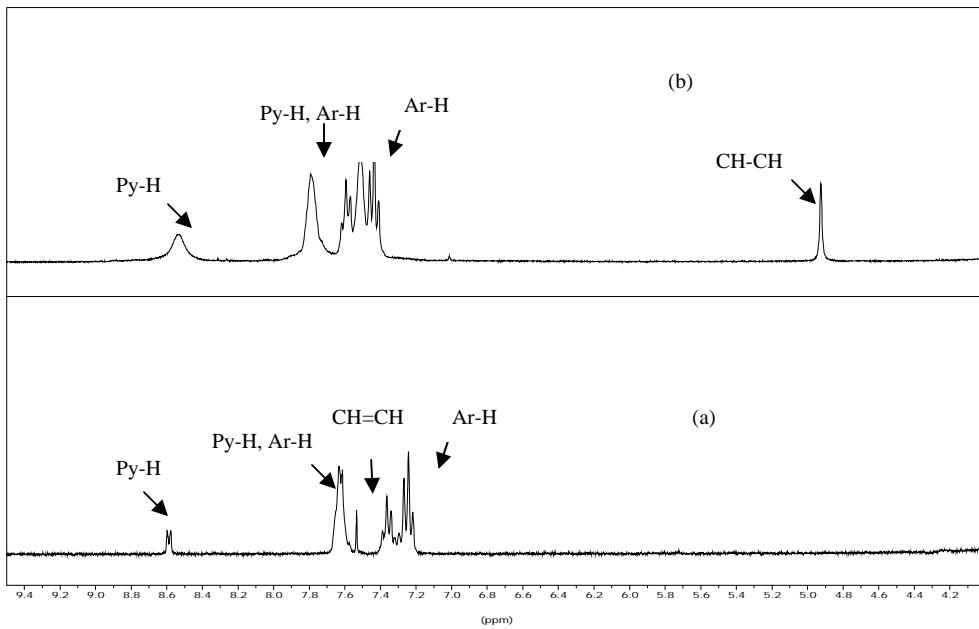


Fig. S3 ¹H NMR spectrum of of **8** (a) before and (b) after UV irradiation in *d*₆-DMSO

H₂bpe .2(NO₃)₂ 27

To a mixture of Cd(NO₃)₂ 4H₂O (0.154 g, 0.5 mmol) and trifluoroacetic acid (1 mmol) in 5 ml of H₂O was added of bpe (0.090 g, 0.5 mmol) in 10 ml of ethanol. The clear solution was filtered and kept for slow evaporation. Colorless pinkish crystals of bpe NO₃ formed after two days was filtered, dried under *vacuo*. The XRPD pattern of the complex matched exactly with the reported crystal structure. Yield= 90 %; (KBr, cm⁻¹): ν = 1627, 1510, 1409, 1379, 1285, 977, 818; ¹H NMR (*d*₆-DMSO, 300 MHz, 298K) δ = 8.91 (d, 4H, Py-H), 8.16 (d, 4H, Py-H), 8.00 (d, 2, CH=CH). Elemental analysis (%) calcd. for C₁₂H₁₂N₄O₆: C, 46.75; H, 3.92, N, 18.17; Found: C, 46.84; H, 3.77; N, 18.00%.

After UV irradiation: The crystals were irradiated for 25 h; Yield= 100 %; (KBr, cm⁻¹): ν = 1637, 1604, 1507, 1419, 1384, 820; ¹H NMR (*d*₆-DMSO, 300 MHz, 298K) δ = 8.57 (d, 4H, Py-H), 7.56 (d, 4H, Py-H), 5.02 (d, 2H, CH-CH). Elemental analysis (%) calcd. for C₁₂H₁₂N₄O₆: C, 46.75; H, 3.92, N, 18.17; Found: C, 46.95; H, 3.95; N, 18.20%.

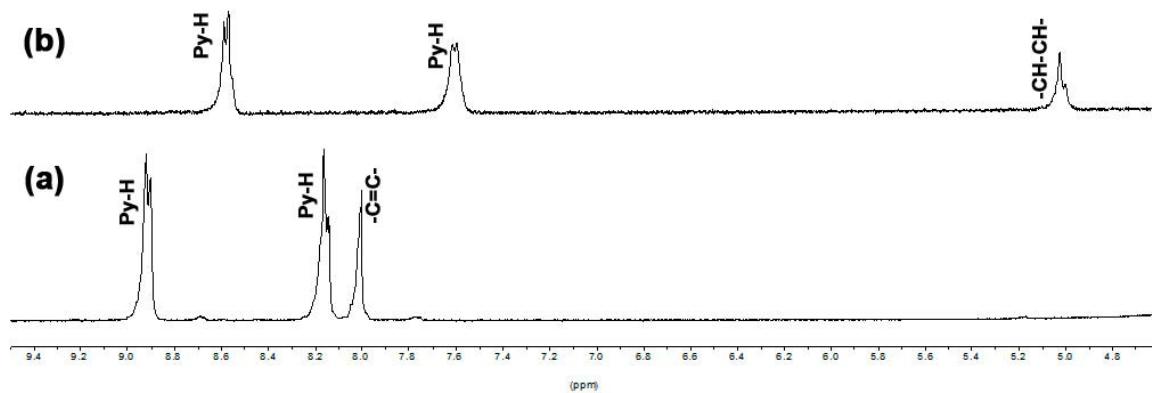


Fig. S4 ¹H NMR spectrum of 27 in *d*₆-DMSO (a) before and (b) after irradiation