ELECTRONIC SUPPLEMENTARY INFORMATION

Chemodosimeteric cyanide sensing in 5,15-Porphodimethene Pd(II) Complex

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Table of contents:

1. Materials and methods

The reagents and materials for synthesis were used as obtained from Sigma - Aldrich chemical suppliers. All solvents were purified and dried by standard methods prior to use. NMR solvents were used as received. The NMR spectra were recorded with Bruker 400 MHz spectrometer with TMS as internal standard. ESI mass spectra were recorded on Bruker, microTOF-QII mass spectrometer. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. Electronic absorption spectra were recorded with Perkin Elmer – Lambda 750 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. The irradiation experiment was performed with Newport, 1918-C model, Xenon source with 135 W power supply. X-ray quality crystal for **1** was grown by the slow diffusion of hexane over CH_2Cl_2 solution of the metal complex similarly slow diffusion of hexane over CH_3CN solution of the metal complex yielded the polymorph of **1**. Single-crystal X-ray diffraction data of **1** were collected on a Bruker KAPPA APEX-II, four angle rotation system, MoKα radiation (0.71073 Å). All experiments were carried out at room temperature (25 ±1°C), unless otherwise mentioned.

2. ^{1}H NMR titrations of 1 with CN^-

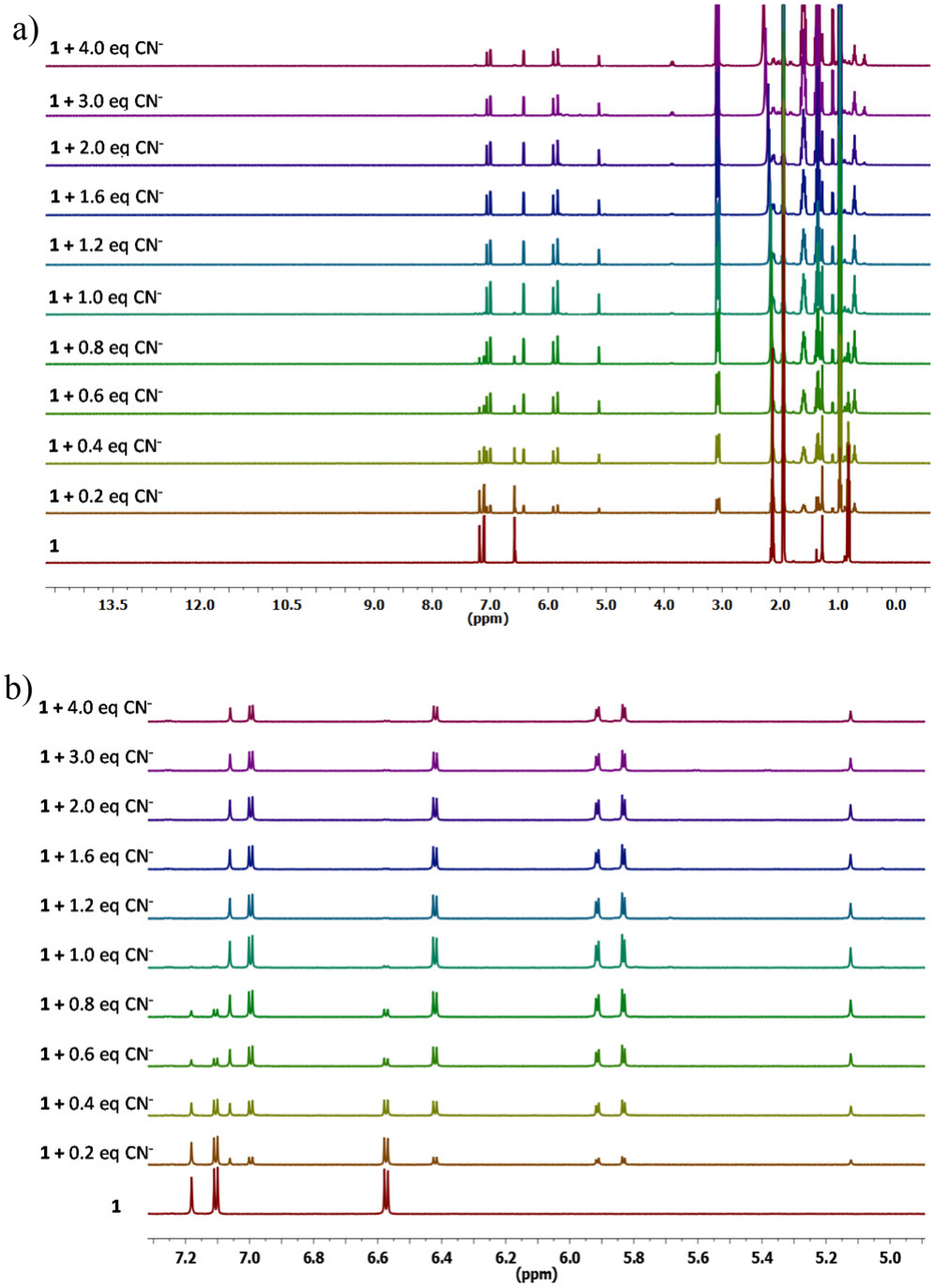

Figure S1. (a) ^{1}H NMR titrations of **1** in CD_3CN upon increasing concentration of tetrabutylammonium cyanide (TBACN) in CD_3CN. (b) Expansion from 5.0 to 7.2 ppm.

3. Absorption spectral analyses of 1 with CN^-

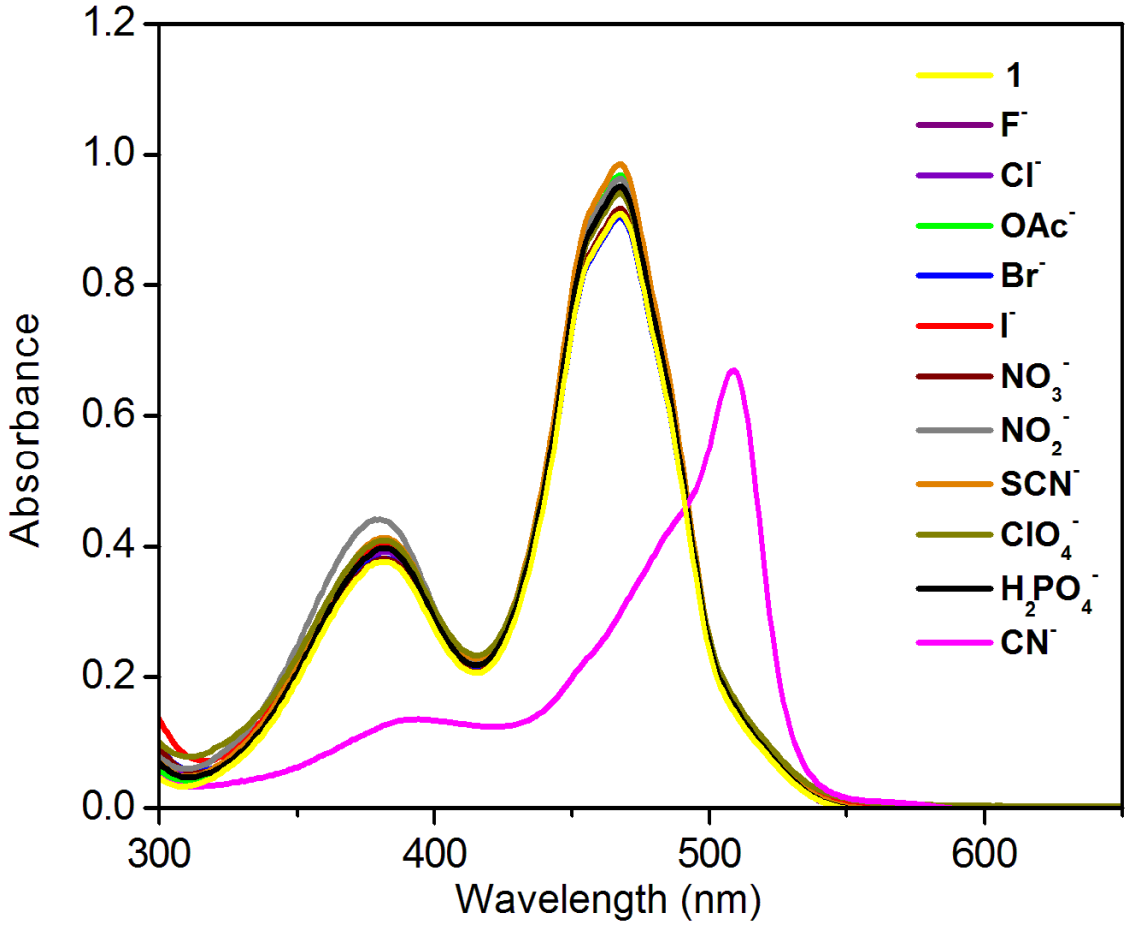

Figure S2: UV-vis absorption spectra of **1** in CH_3CN upon addition of various anions.

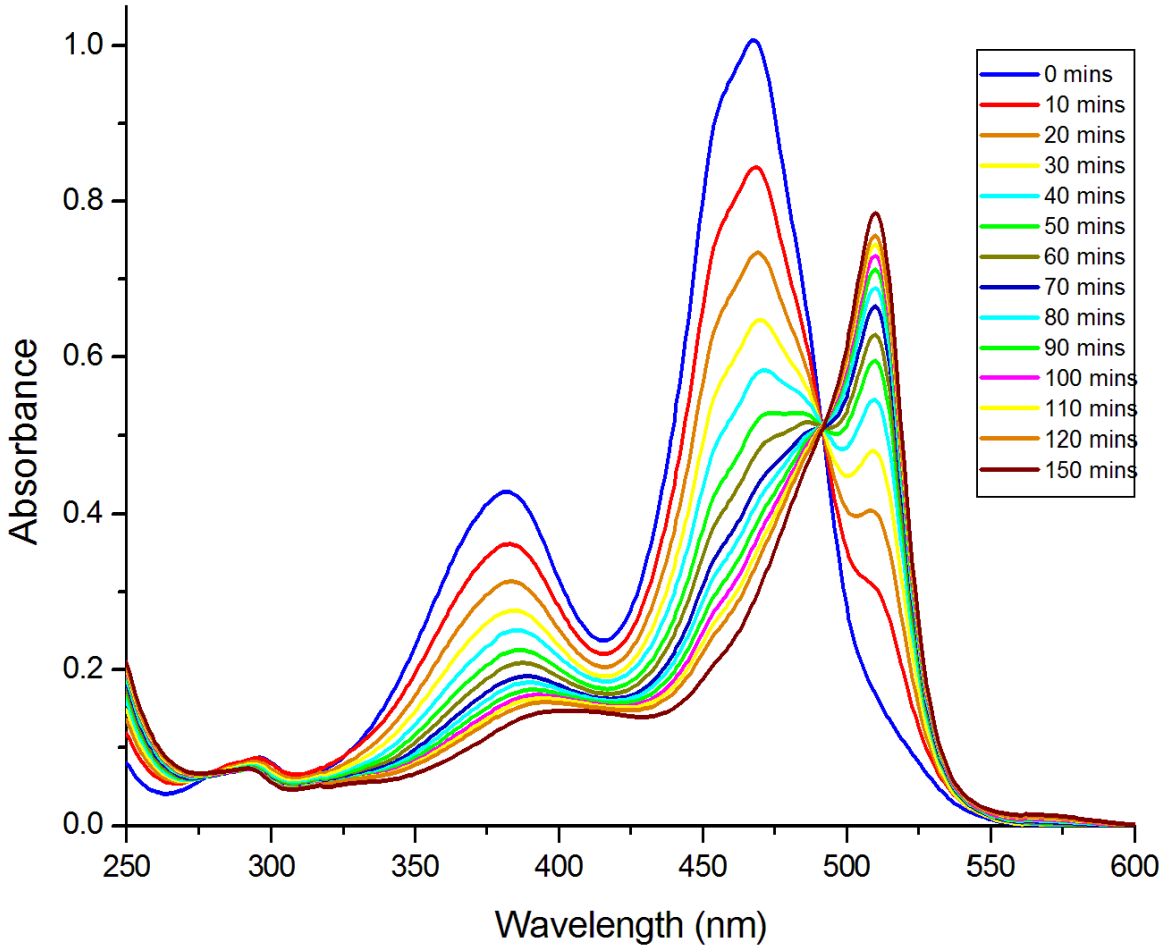

Figure S3. Time dependent electronic absorption spectral changes of **1** (20 μM) in CH_3CN upon addition of 25 equiv. of CN^-.

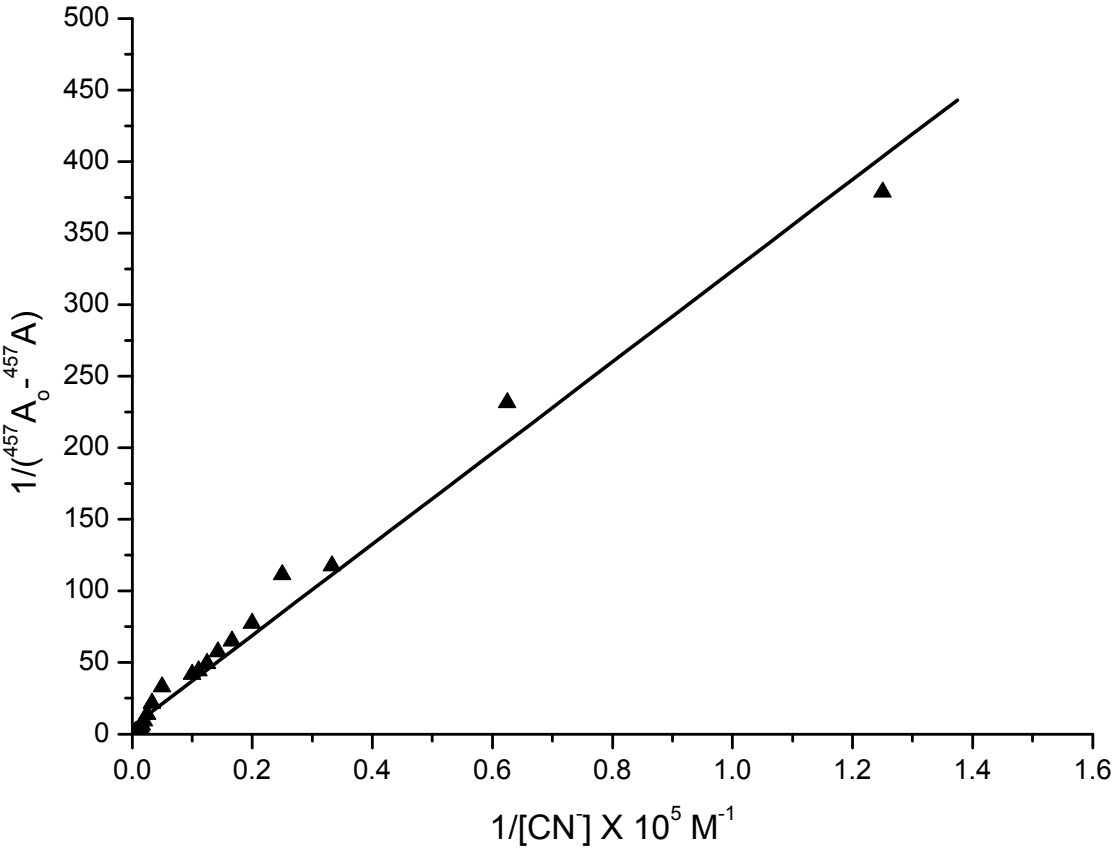

Figure S4. Benesi-Hildebrand plot of **1** with CN^- in CH_3CN.

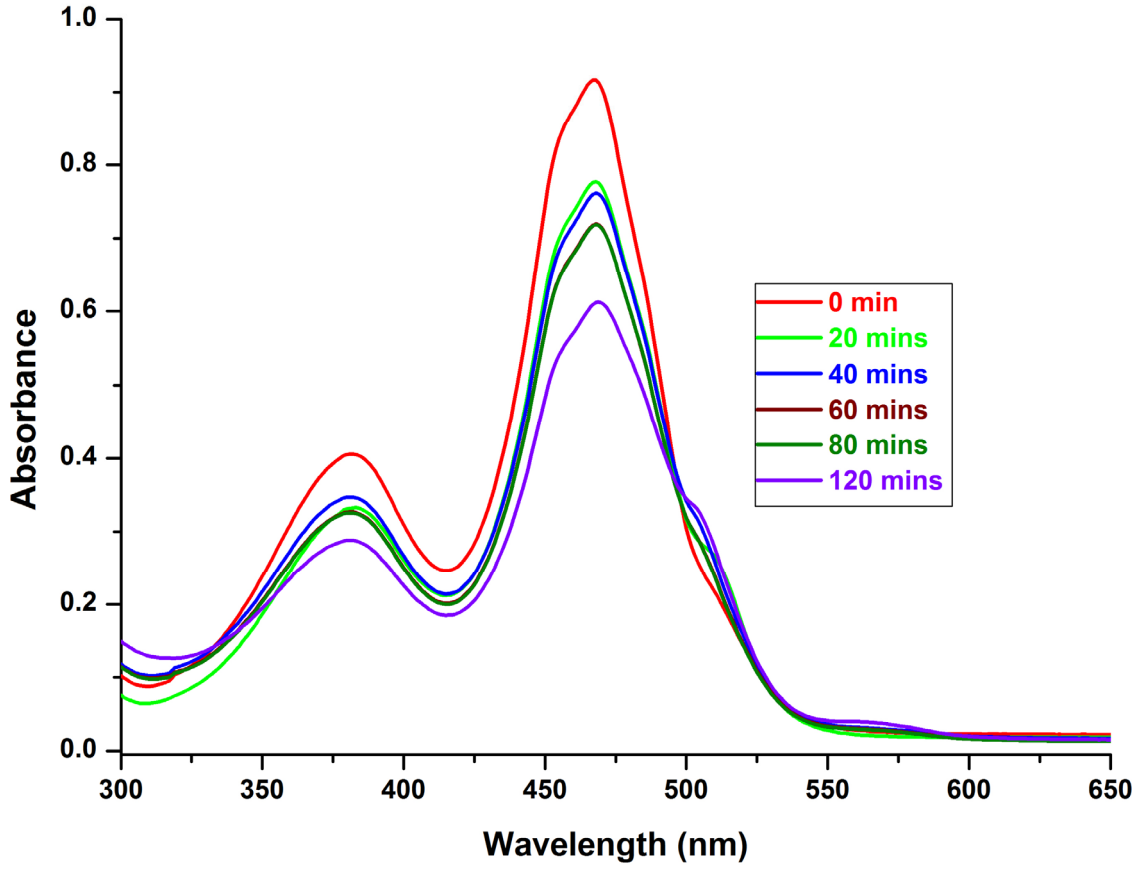

Figure S5. Time dependent electronic absorption spectral changes of **1** (20 μM) in CH_3CN upon addition of 25 equiv. of CN^- under irradiation at 310 nm.

4. ESI-MS spectra of [1.CN]$^-$ adduct:

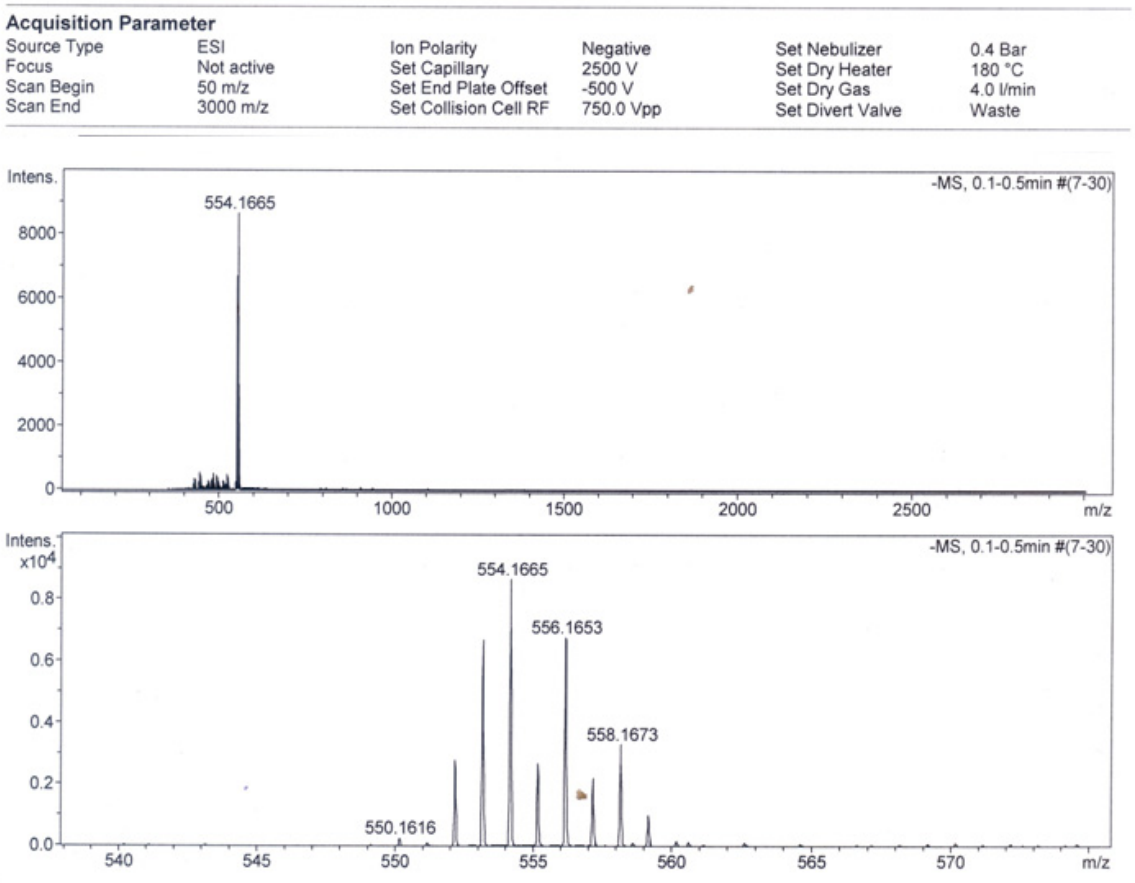

Figure S6. ESI-MS spectra of [**1.CN**]$^-$ adduct recorded in the negative mode.

5. Single Crystal X-ray Structure and Analysis of 1:

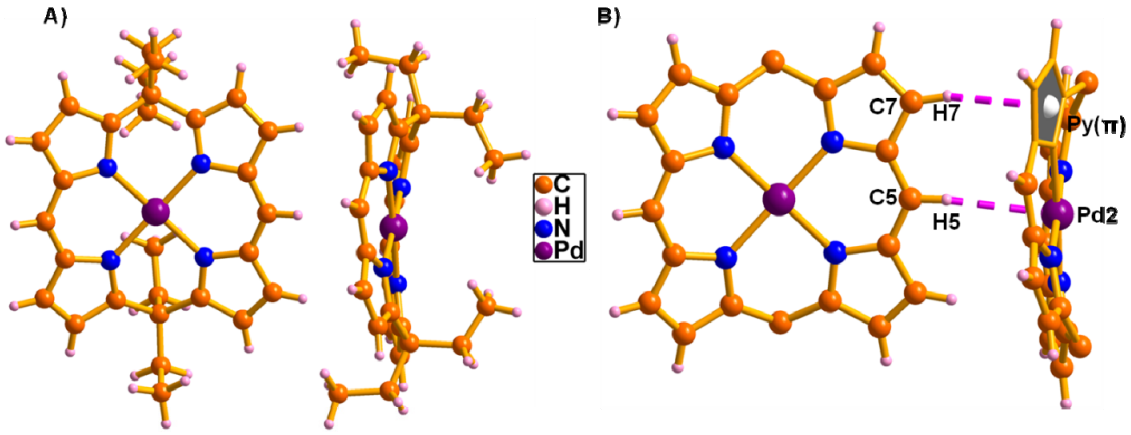

Figure S7. Single crystal X-ray structure of **1** by slow evaporation of CH_2Cl_2/*n*-Hexane. A) Top view and B) side view with intermolecular hydrogen bonding interactions. The distances and angles of C5-H5…Pd2 and C7-H7…Py(π) are 2.89 Å, 157° and 1.70, Å, 162° respectively. The units which are not involved in the hydrogen bonding interactions are omitted for clarity in the side view.

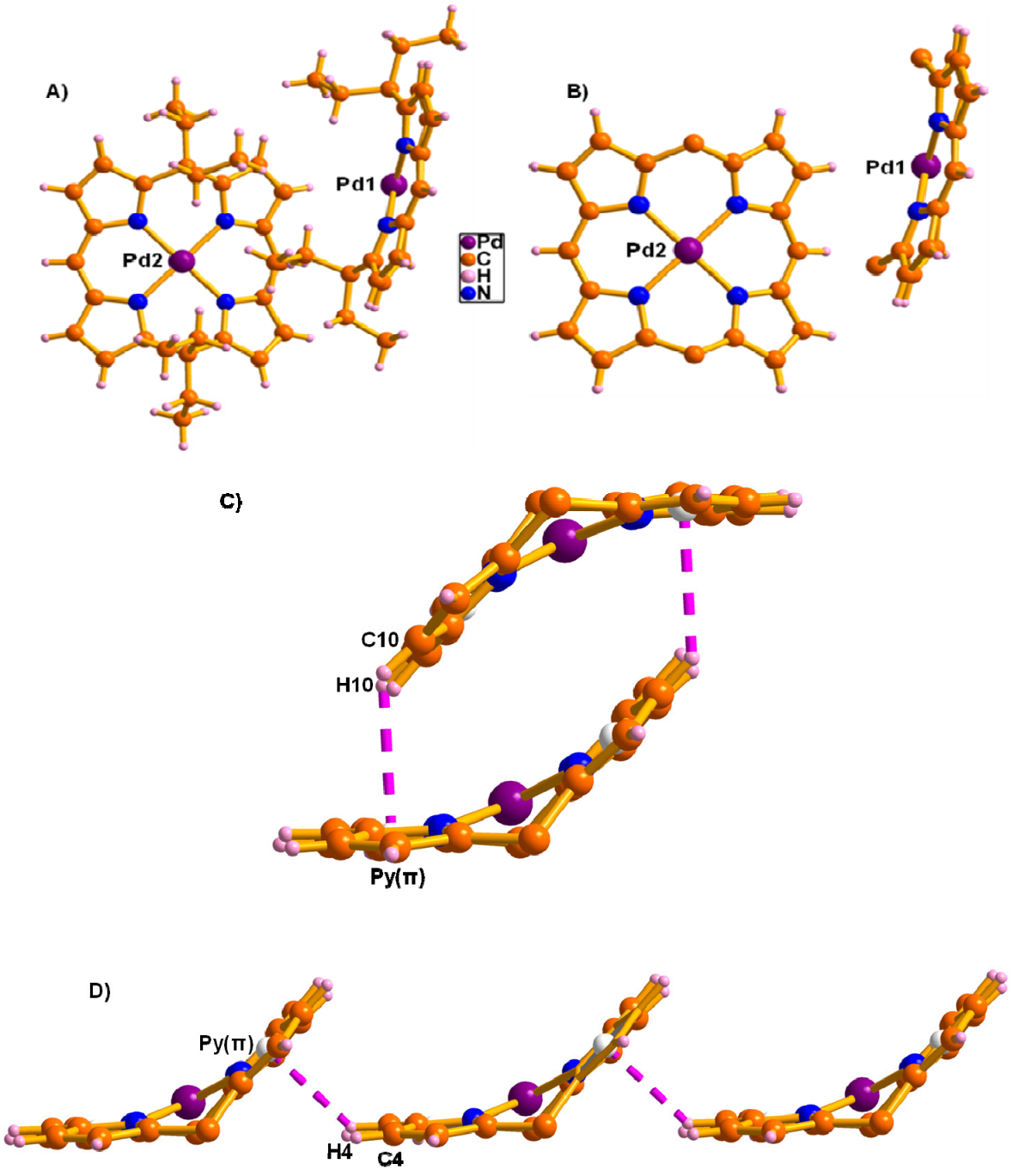

Figure S8. Single crystal X-ray structure of **1** by slow evaporation of CH_3CN/*n*-Hexane. A) Top view, B) side view, C) self-assembled dimer and D) 1-D array. The *meso*-diethyl units are omitted for clarity in the side view.

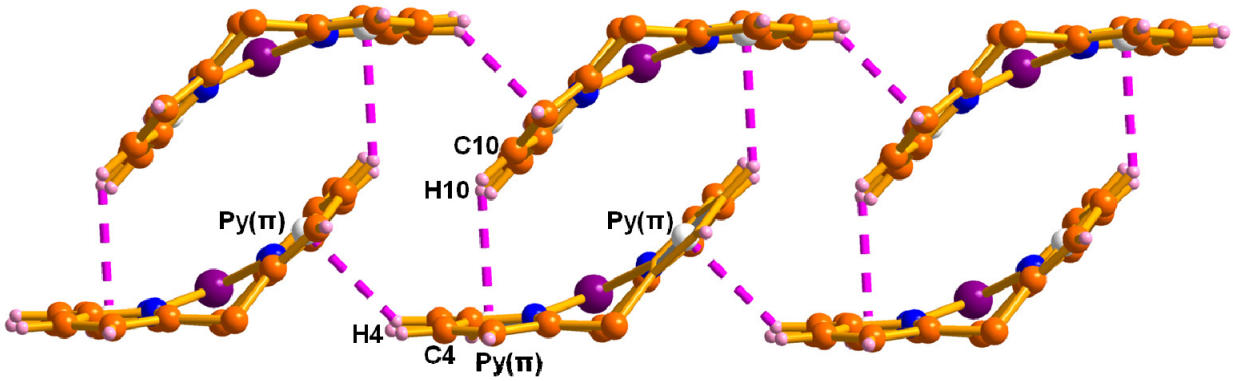

Figure S9. 1-D supramolecular assembly of **1** by slow evaporation of CH_3CN/*n*-Hexane.

6. Crystal data for 1:

	1 (CH_2Cl_2/*n*-Hexane)	**1 (CH_3CN/*n*-Hexane)**
Formula	$C_{56}H_{60}N_8Pd_2$	$C_{56}H_{60}N_8Pd_2$
M/g mol^{-1}	1057.92	1057.92
T/K	293(2)	293(2)
Crystal dimensions/mm^3	0.20 x 0.05 x 0.05	0.13 x 0.07 x 0.06
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a/Å	16.5817(15)	8.250(5)
b/Å	14.4709(12)	14.764(5)
c/Å	20.188(2)	19.582(5)
α/°	90.00	88.932(5)
β/°	99.123(5)	89.487(5)
γ/°	90.00	74.757(5)
V/Å^3	4783.0(8)	2300.8(17)
Z	4	2
ρ_{calcd}/mg m^{-3}	1.469	1.527
μ/mm^{-1}	0.799	0.831
F(000)	2176	1088
Reflns. collected	7299	2704
Indep.reflns.[R(int)]	8420[0.0517]	10568[0.0855]
Max/min transmission	0.922 and 0.801	0.9518 and 0.8997
Data/restraints/parameters	8420/0/604	10568/0/595
GOF on F^2	1.090	1.002
Final R indices[$I > 2\sigma(I)$]	R1 =0.0399, wR2 = 0.1004	R1 =0.0493, wR2 = 0.0908
R indices (all data)	R_1=0.0707	R_1=0.0967
Largest diff peak and hole [e Å^{-3}]	0.787 and -0.707	0.783 and -0.827

Table S1 Crystal data for **1** (CH_2Cl_2/*n*-Hexane) and **1** (CH_3CN/*n*-Hexane)

CCDC-930501 for **1** (CH_2Cl_2/*n*-Hexane) and CCDC-1006605 for **1** (CH_3CN/*n*-Hexane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.