Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

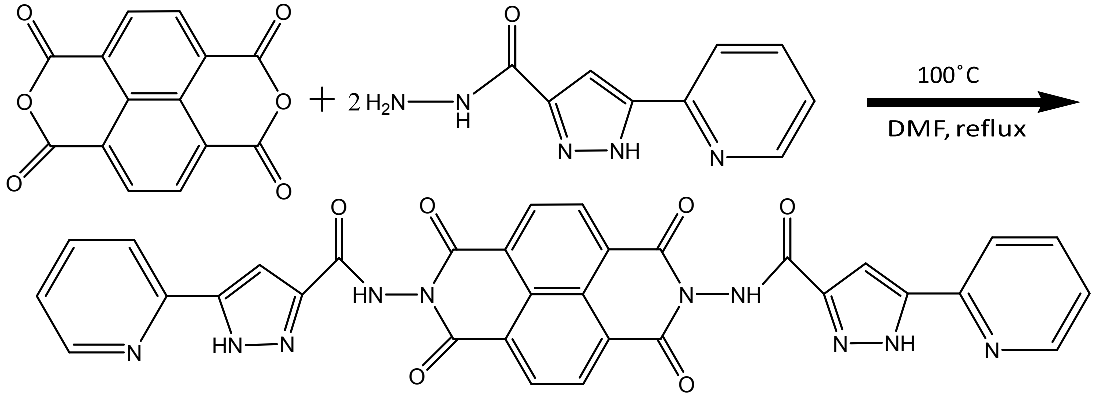
Experimental Section:

General Information: In the present work, all chemicals used were analytical grade, and were obtained from commercial sources more importantly $cTiO_2$ (commercial TiO_2) is anatase Titanium (IV) oxide and purchased from Sigma Aldrich and used without further purification unless otherwise stated. Elemental analysis (C, H, and N) were performed using a 2400 Series-II CHN Analyzer, Perkin–Elmer, USA; FT-IR spectra of the samples were recorded in the range of 400–4000 cm^{-1} on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. ^1H NMR was carried out by Bruker Spectrometer operating at 400 MHz in DMSO-d_6 solvent; mass spectrum was collected by Micro mass Q-Tof Micro instrument. UV-Visible and UV-Vis diffuse reflectance spectra (DRS) were recorded at ambient temperature on a Cary-500 UV-Vis Spectrophotometer along with the usage of different compartment for DRS; Powder X-ray diffraction (PXRD) measurement was characterized using a Bruker AXS diffractometer (D8 advance) using Cu-Kα radiation (λ= 1.5406 Å), a generator voltage of 40 kV and current 30 mA . Sample was scanned in the range of 2θ= 0-100° with the scan rate 1s/step. The HRTEM micrograph of the sample was prepared by taking acetone dispersion of TiO_2 on the carbon coated copper grid and drying at room temperature in air followed by vacuum. High resolution transmission microscopy were carried by JEOL 2010EX operated at an accelerating voltage of 200 kV fitted with a CCD camera. GC analysis were performed on Perkin-Elmer gas chromatograph clarus-580 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 mm) using Argon as carrier gas.

Synthesis of (Ligand) ***N,N'-di-(3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide) naphthalene 1,4,5,8-tetracarboxilic acid bisimide*** **(PPNB):**

0.268 g (0.1 mM) of 1,4,5,8 Naphthalenetetracarboxylicdianhydride and 0.406 g (0.2 mM) 3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide was taken in 5 ml of N,N'-Dimethyl formamide solvent. Then the reaction mixture was heated at 100˚ c for 12 hours. After cooling the reaction mixtures, 20 ml of cold methanol solution was added and stirred for 1 hour. Finally a deep yellow precipitate was obtained which was filtered and washed with methanol and dried in air. (Yield: 82%). ^1H NMR (400 MHz, DMSO-d_6) ; δ (PPM) = 14.28 (s, 2H, 3-pyrazole), 11.20 (d, 2H, 2-pyridine), 8 .83 (s, 4H, NDI), 8.67 (s, 2H, 2 N-H amide), 8.01-7.93 (m, 2H, 2-pyridine, o), 8.01-7.93 (m, 2H, 2-pyridine, p), 7.45-7.41 (m, 2H, 2-pyridine), 7.45-7.41 (s, 2H, 3-pyrazole). Elemental analysis for ligand PPNB, $C_{32}H_{18}N_{10}O_6$; (calculated): C: 60.22, H: 2.84, N: 21.94; (found): C: 59.75, H: 2.94, N: 21.39. IR (KBr pellet):

3361(m, νN-H), 1705 (s, νC=O), 1350 (s, νC-N), 1449 (m, νC-C), 871(m, γCH2) (Fig. S1a). MALDI-TOF-MS: *m/e 639.30 (M^+)*, 661.26 (M^+ + Na).



N,N'-di-(3-(pyridin-2-yl)-1H-pyrazole-5-carbohydrazide) naphthalene 1,4,5,8-tetracarboxilic acid bisimide (PPNB).

Synthesis of (complex) ***N,N'-di-(3-(pyridine-2-yl)-1H-pyrazole-5-carbohydrazide) naphthalene 1,4,5,8-tetracarboxilic acid bisimide tetra Nickel(II)*** **(Ni-PPNB):**

To a mixture of 0.0365 g (0.01 mM) of nickel perchlorate and 0.0319 g (0.005 mM) of the PPNB ligand was taken in N,N'-dimethyl acetamide and dimethyl sulfoxide (1:1 ratio) solvent and then the reaction mixture was heated at 80˚c for 3 days. After slow cooling of the mixture deep red needle shaped crystals were collected which were suitable for X-ray diffraction. The complex was then washed with methanol and dried in the air. (Yield: 55%). Elemental analysis for complex $C_{78} H_{72} N_{20} Ni_4 O_{19} S_7$; (calculated %): C: 45.59, H: 3.50, N: 13.36; (found %): C : 45.03, H : 3.44, N : 12.92. IR (KBr pellet): 3361(m, νN-H), 1687 (s, νC=O), 1287 (s, νC-N), 1440 (m, νC-C), 1032 (m, γCH2) (**Figure S1b.**).

Synthesis of TiO_2:

TiO_2 nanocrystals were prepared by typical hydrolysis method. First 50 mL of 1M HCl (aqs.) solution (pH≥3.5) was taken in a 250 mL round bottom flask. 1 mL of Triton X was added drop wise into the solution and stirred it for 5 min to make the solution completely homogeneous. Then 5 mL Titanium (IV)-butoxide was added drop wise into the solution and it was then heated under 40 °C for 24 h using oil bath and reflux condenser with continuous flowing of water. The white particles were visible inside after completion of the reaction. Then it was filtered, washed with water and ethanol twice and dried at 100 °C for 10h. The yellow-white powder was then calcined at

400 ºC for 5 h under aerobic condition. IR (KBr pellet): 507(broad, s, νTi-O) (Fig S1a and S1b). In XRD analysis (Fig S6) diffraction angles (2θ) are 25.3º, 38.1º, 48º, 54º, 55.5º and 62.8º.

Synthesis of platinized TiO_2 (1 wt %):

Platinized TiO_2 was prepared by a photochemical reduction method. In a 100 ml round-bottomed flask, 1 gm TiO_2 was dispersed in 20 ml methanol with adequate time of ultrasonication. To this solution, H_2PtCl_6 (0.25 ml, 8 wt% aqueous solution) was slowly added. Then, the reaction mixture was irradiated for 1 h under 450 W Xe-lamp. H_2PtCl_6 was reduced to form Pt nanoparticles during the reaction, causing a change in color of the material from pale yellow to grayish. The resultant composites were retrieved by centrifugation, washed five times with excess methanol and dried under vacuum. The as synthesized platinized samples are designated as Pt/cTiO_2 and Pt/sTiO_2.

Synthesis of PPNB-Pt/c,sTiO_2, Ni-PPNB-Pt/c,sTiO_2:

PPNB and Ni-PPNB sensitized TiO_2 were prepared by using simple self assembly method.[1] Optimized amount of dyes (PPNB, Ni-PPNB) were sonicated in a mixture of 1:1 ethanol (10mL) and acetonitrile (10 mL) in a 100 mL round bottomed flask for 30 min. After then 100 mg TiO_2 was added in the dye suspension and stirred for 12 h at room temperature in dark condition. It was then filtered, washed several times with DI water and dried at 50 ºC for 5 h and labeled as PPNB-Pt/sTiO_2(**II**) and Ni-PPNB-Pt/sTiO_2(**IV**).The identical composites ware prepared using commercial p25 TiO_2 and labeled as PPNB-Pt/cTiO_2(**I**) and Ni-PPNB-Pt/cTiO_2.(**III**)

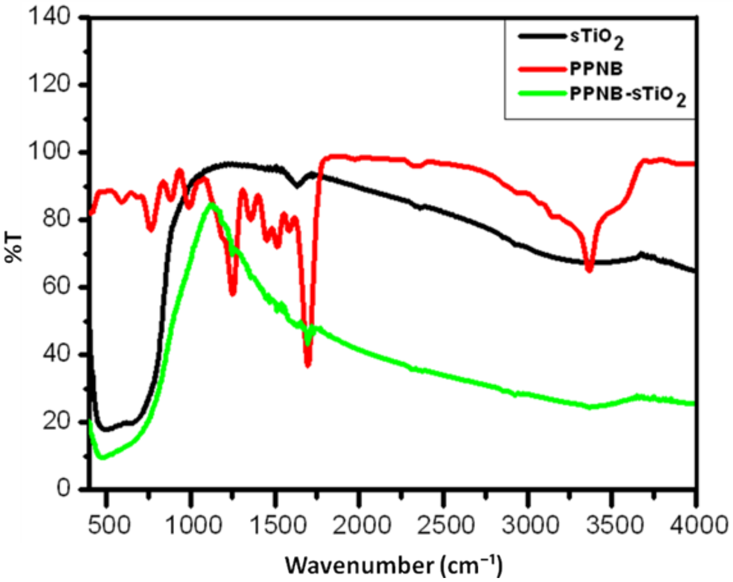


Figure S1a. FT-IR of sTiO_2, PPNB and PPNB-sTiO_2.

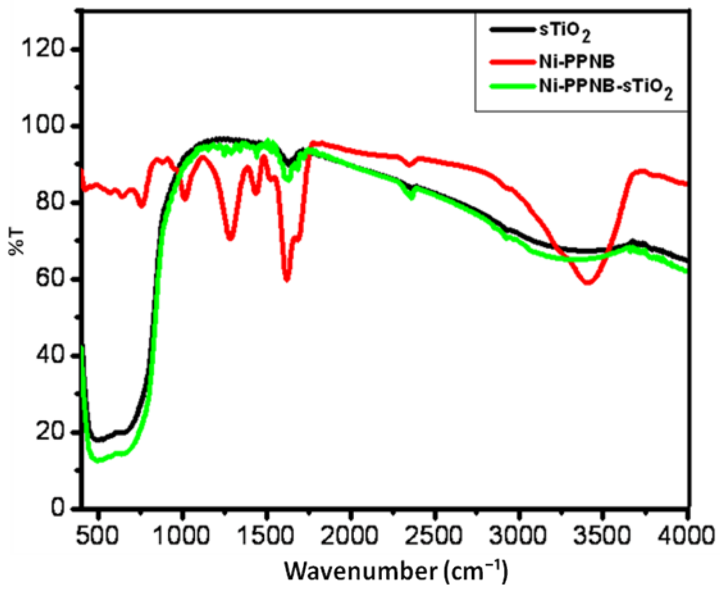


Figure S1b. FT-IR of $sTiO_2$, Ni-PPNB and Ni-PPNB-$sTiO_2$

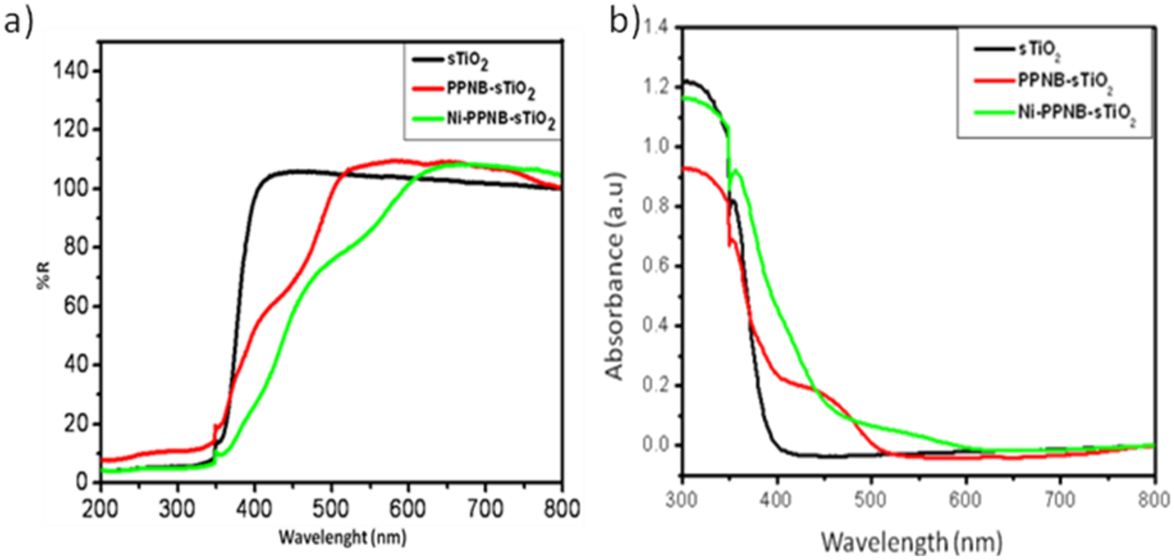


Figure S2a. UV-Vis DRS spectra of $sTiO_2$, PPNB-$sTiO_2$ and Ni-PPNB-$sTiO_2$ and **S2b.** Same in the absorption mode.

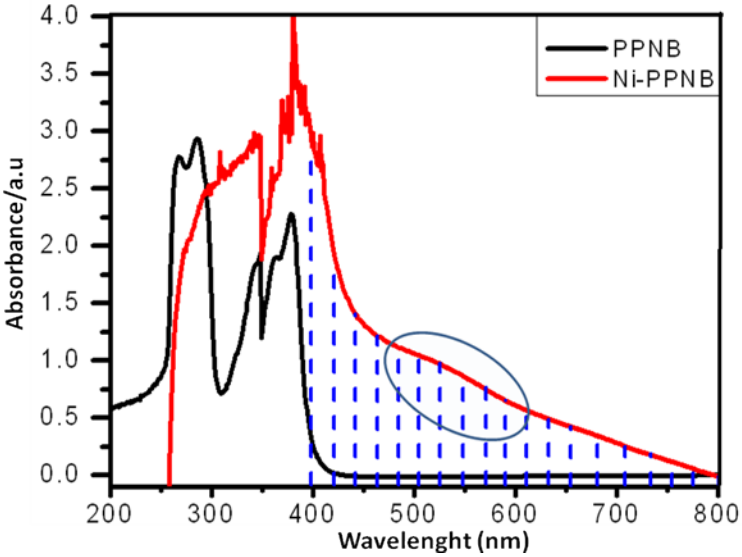


Figure S3. UV-Vis absorption spectra of PPNB and Ni-PPNB

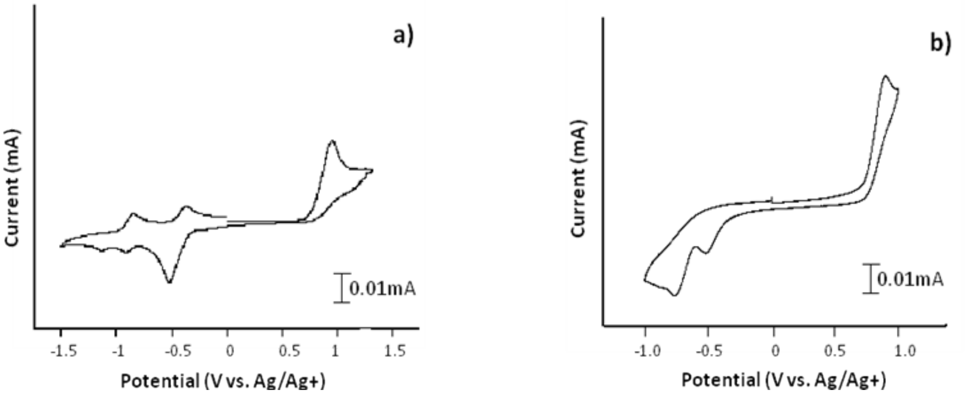


Figure S4. Cyclic voltammogram of (a) PPNB and (b) Ni-PPNB

Table S1.

Dyes	*E*o-o (eV)(1)	*E*ox1/2 (V)(2)	HOMO (eV)	LUMO (eV)
Ni-PPNB	2.82	0.85	-5.86	-3.04
PPNB	3.18	0.87	-5.89	-2.71

(1) o-o transition energies were measured at the onset of the absorption spectra. (2) Oxidation potential were measured using Fc/Fc+ as standard and 0.01 M Bu_4NBF_4 in Pt and Ag/Ag+ as the supporting electrolyte solution, working and reference electrode in water DMSO, working and reference electrode respectively. Scan rate 20 mV/S

was applied throughout the experiment. HOMO values were calculated using potential value of oxidative waves. LUMO values were calculated by addition of HOMO values with the *E*o-o.

Table S2. Apparent Quantum Yield (AQY) of H_2 generation of different catalysts under different SED

Catalyst	SED	AQY
III	TEOA	**2.16**
III	DEOA	**4.71**
III	MEOA	**0.82**
III	MeOH	**4.32**
IV	TEOA	**1.4**
IV	DEOA	**3.2**
IV	MEOA	**3.44**
IV	MeOH	**3.03**

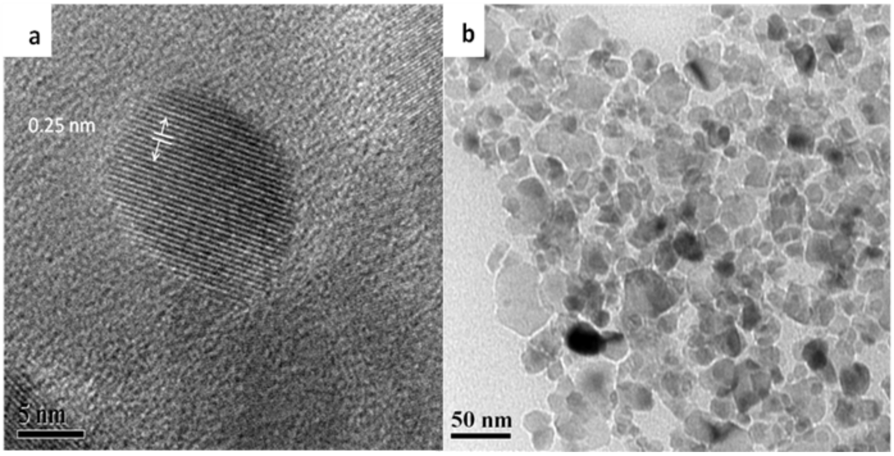


Figure S5. (a) HRTEM lattice fringes image of TiO_2 nanocrystal. (b) HRTEM image of hexagonal shaped TiO_2 nanocrystals

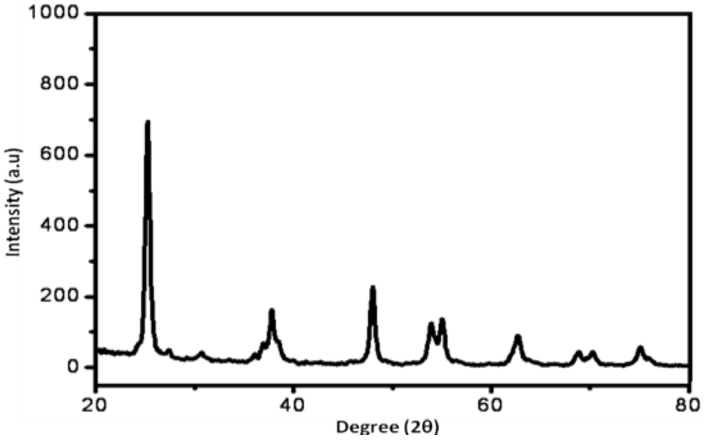


Figure S6. Powder X-ray diffraction (PXRD) pattern of TiO_2 nanocrystal

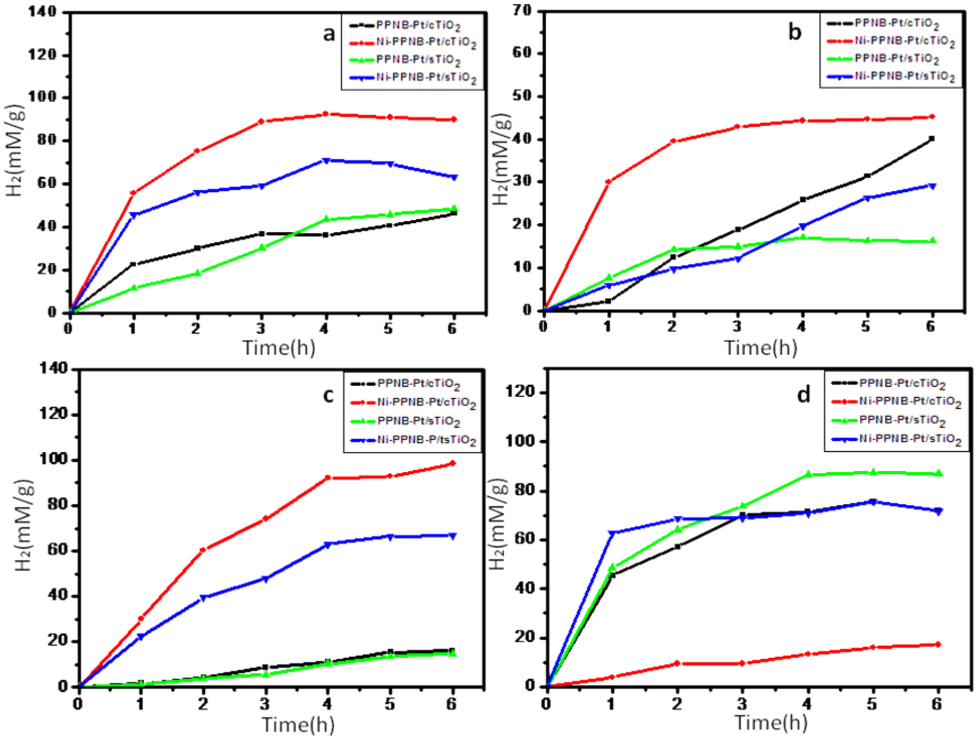


Figure S7. Time courses of photocatalytic H_2 evolution over catalyst 10 mg **I, II, III** and **IV** (0.25 μmol dye) in 20 mL solution (graph a, b, c and d corresponds to amount of H_2 evolution in 10 V% aqs solution of MeOH, TEOA, DEOA and MEOA respectively) under visible light irradiation (λ > 400 nm).; light source, Xe lamp (450 W).

X-ray crystallography:

X-ray diffraction intensity was collected at 120 K on Bruker APEX-2 CCD diffractometer using Mo-K_α radiation and processed using SAINT. The structure was solved by direct methods in SHELXS and refined by full matrix least-squares on F^2 in SHELXL.[1] The non-hydrogen atoms were refined with anisotropic displacement parameters except for disordered DMSO molecule. The disordered DMSO molecule was refined by constraints using the PART command, with a total occupancy of 1. The PLATON/SQUEEZE programme[2] was used to remove the scattering contribution from any residual electron density found in the lattice.

Table S3. Crystallographic data and refinement parameters for Ni-PPNB

Parameters	**Compound: Ni-PPNB**
Empirical formula	$C_{72}H_{52}N_{20}Ni_4O_{16}S_4$
Formula weight	**1816.42**
Crystal system/Space group	**Triclinic/*P*-1**
Unit cell dimensions	**a = 13.030(9) Å, b = 13.687(10) Å, c = 15.078(10) Å** **α= 91.61(2)°, β= 107.895(19)°, γ= 102.39(2)°.**
Volume	**2487(3) Å^3**
Z	**1**
Reflections collected	**22921**
Unique reflections	**8970**

Observed reflections $[I>2\sigma(I)]$	**5670**
R_{int}	**0.0826**
wR2	**0.2170**
CCDC No.	**971437**

Table S3. Selected bond lengths and bond angles of Ni-PPNB

Bond lengths		**Bond angles**	
Ni$_1$….N$_{2A}$	**1.993(5)**	**N$_{2A}$….Ni$_1$….N$_2$**	**89.31(19)**
Ni$_1$….N$_2$	**2.023(4)**	**N$_{2A}$….Ni$_1$….O$_{1SB}$**	**99.6(5)**
Ni$_1$….O$_{1SB}$	**2.120(17)**	**N$_2$….Ni$_1$….O$_{1SB}$**	**91.7(5)**
Ni$_1$….O$_{1S}$	**2.130(5)**	**N2A….Ni1….O1S**	**91.3(2)**
Ni$_1$….N$_1$	**2.131(5)**	**N2….Ni1….O1S**	**88.79(19)**
Ni$_1$….O$_{1SA}$	**2.168(9)**	**O$_{1SB}$….Ni$_1$….O$_{1S}$**	**169.1(5)**
Ni$_1$….N$_{1A}$	**2.169(5)**	**N$_{2A}$…..Ni$_1$….N$_1$**	**167.71(17)**
Ni$_2$….N$_3$	**1.878(5)**	**N$_2$….Ni$_1$….N$_1$**	**78.42(18)**
Ni$_2$….N$_{3A}$	**1.889(5)**	**O$_{1SB}$….Ni$_1$….N$_1$**	**80.2(5)**
Ni$_2$….N$_{4A}$	**1.932(5)**	**O$_{1S}$….Ni$_1$….N$_1$**	**89.22(19)**
Ni$_2$….N$_{10}$	**1.940(4)**	**N$_{2A}$….Ni$_1$….O$_{1SA}$**	**91.5(3)**
		N$_2$….Ni$_1$….O$_{1SA}$	**98.1(3)**
		O$_{1SB}$….Ni$_1$….O$_{1SA}$	**10.4(5)**
		O$_{1S}$….Ni$_1$…..O$_{1SA}$	**172.6(2)**
		N$_1$….Ni$_1$….O$_{1SA}$	**89.5(3)**
		N$_{2A}$….Ni$_1$….N$_{1A}$	**78.36(18)**
		N$_2$….Ni$_1$….N$_{1A}$	**167.39(19)**

	O$_{1SB}$….Ni$_1$….N$_{1A}$	**93.0(5)**
	O$_{1S}$….Ni$_1$….N$_{1A}$	**88.8(2)**
	N$_1$….Ni$_1$….N$_{1A}$	**113.93(18)**
	O$_{1SA}$….Ni$_1$….N$_{1A}$	**85.0(3)**
	N$_3$….Ni$_2$….N$_{3A}$	**94.9(2)**
	N$_3$….Ni$_2$….N$_{4A}$	**175.0(2)**
	N$_{3A}$….Ni$_2$….N$_{4A}$	**80.9(2)**
	N$_3$….Ni$_2$….N$_{10}$	**80.59(19)**
	N$_{3A}$….Ni$_2$….N$_{10}$	**173.3(2)**
	N$_{4A}$….Ni$_2$….N$_{10}$	**103.83(19)**

References:

1. E. Bae, W. Choi, J. Park, H. S. Shin, S. B. Kim, J. S. Lee, *J. Phys. Chem. B.* 2004, **108,** 14093
2. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.
3. (a) A. L. Spek, Acta Crystallogr., Sect. A, 1990, 46, C34; (b) G. Bernardinelli and H. D. Flack, Acta Crystallogr., Sect. A: Found. Crystallogr., 1985, 41, 500–511; (c) H. D. Flack, Acta Crystallogr., Sect. A: Found. Crystallogr., 1983, 39, 876–881.