Ni(II)-MOF: reversible guest adsorption and heterogeneous catalytic property for silylcyanation of aromatic aldehydes

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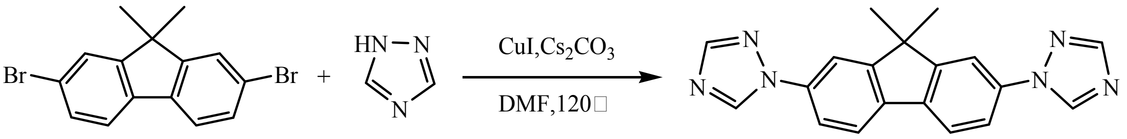
I. L and compound 1:

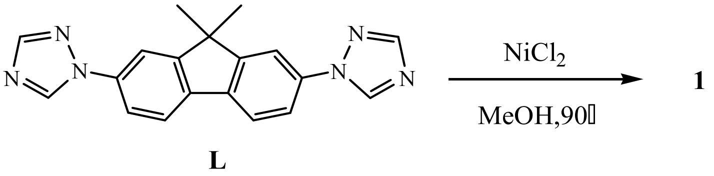
Synthesis of L



Scheme S1. Synthesis of **L**.

A DMF (20 mL) solution of 2,7-Dibromo-9,9-dimethylfluorene (3.52g, 10mmol), 1,2,4-triazole (1,93g, 28mmol), $Cs_2(CO_3)$ (13.03g, 40mmmol) and CuI (0.762g, 4mmol) was heated at 120°C. The reaction was monitored by TLC. The resulted solution was poured into water (300 mL). The product was purified by column chromatography on silica gel (CH_2Cl_2 : EtOAc = 1 : 1) to afford **L** as yellow crystalline solid in 70 % yield. IR(KBr pellet cm^{-1}): 3099 (m), 2966(w), 2929(vw), 1611(m), 1588(s), 1478(m), 1216(s), 1151(s), 988(s), 885(s), 815(vs), 673(vs). ^1H NMR (300 MHz, $CDCl_3$, 25℃, TMS, ppm): δ = 8.66 (s, 2H, $-C_2H_2N_3$), 8.16(s, 2H, $-C_2H_2N_3$), 7.85-7.87(d, *J* = 6.0Hz, 2H, $-C_6H_3$), 7.81(s, 2H, $-C_6H_3$), 7.66-7.69(d, *J* = 8.2Hz, 2H, $-C_6H_3$), 1.60 (S, 6H, $-CH_3$). Elemental Analysis(%): calcd. for $C_{19}H_{16}N_6$: C 69.51, H 4.88, N 25.61; Found: C 69.47, H 4.83, N 25.70.

Synthesis of 1



Scheme S2. Synthesis of **1**.

L (3.3mg，0.01mmol), $NiCl_2$ (1.8mg，0.0075mmol) and MeOH (2 mL) were sealed in a 5-mL glass tube. The mixture was heated at 90°C for 72 hours under autogenous pressure. After the mixture was allowed to cool to room temperature (50 hours), light blue rod-like crystals were isolated from the tube in 78 % yield (based on L). IR(KBr pellet cm^{-1}): 3143(w), 3064(w), 2955(w), 1519(s), 1483(m), 1465(m), 1215(s), 1084(s), 979(vs), 809(vs), 669(vs), 654(m) Elemental Analysis(%): calcd for $C_{38}H_{32}N_{12}NiCl_2$: C 58.01, H 4.07, N 21.37; Found: C 57.59, H 4.46, N 20.50.

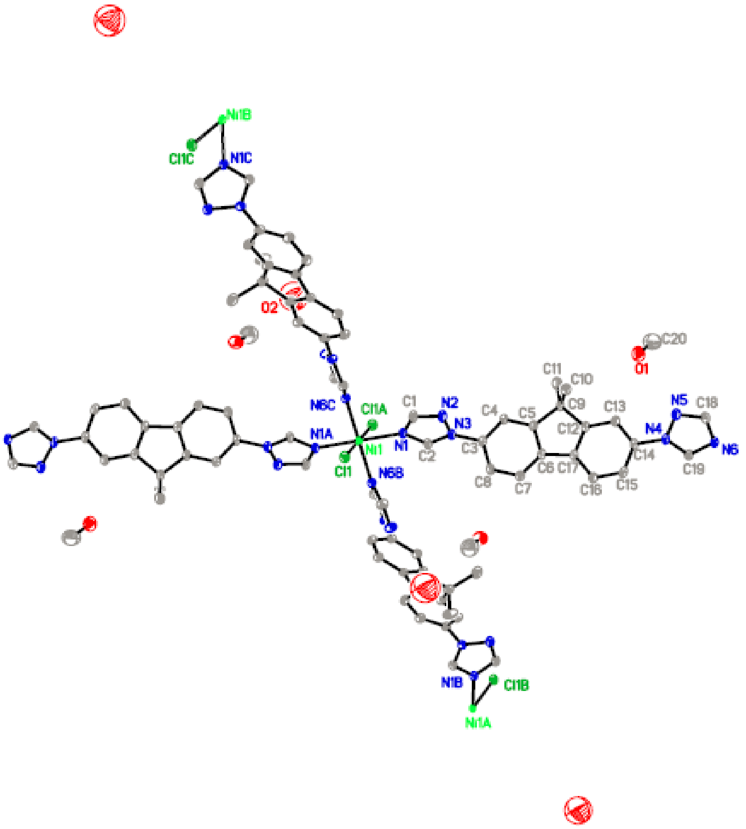


Fig. S1 The ORTEP figure of $NiL_2Cl_2{\cdot}2CH_3OH{\cdot}0.5H_2O$ (**1**).

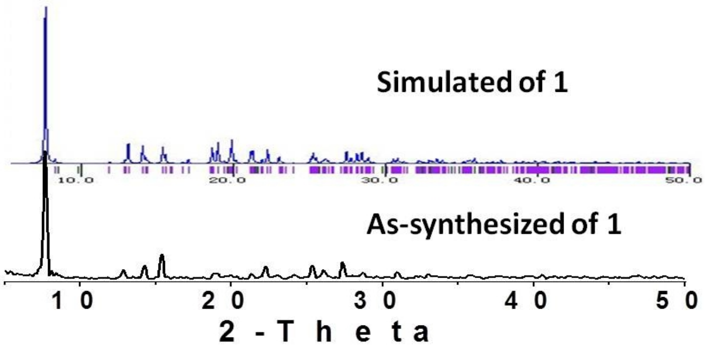


Fig. S2 XRPD patterns of **1**, indicating that compound **1** was obtained in pure phase.

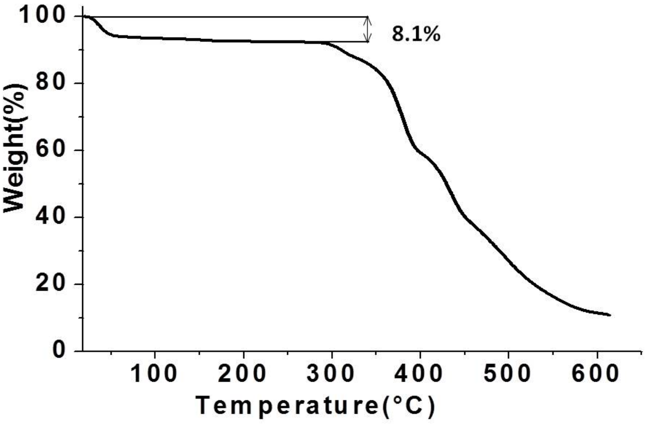


Fig. S3 TGA trace of **1.** The observed solvent mass loss is 8.1 % (calculated 8.5%).

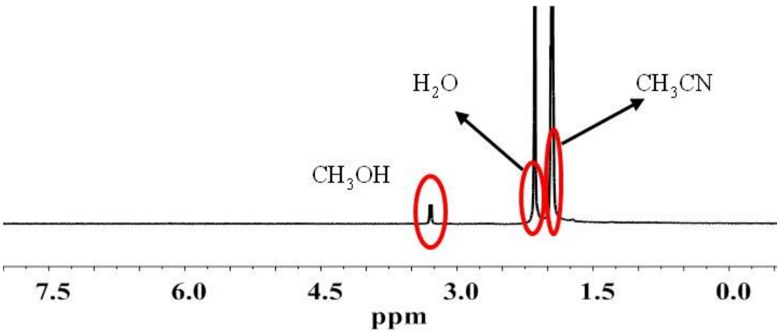


Fig. S4 ^{1}H NMR spectrum of the CD_3CN extract of **1**.

II. Compound 2:

Synthesis of 2. The crystals of **1** were heated at 100°C for 4 h to generate desolvated compound **2**.

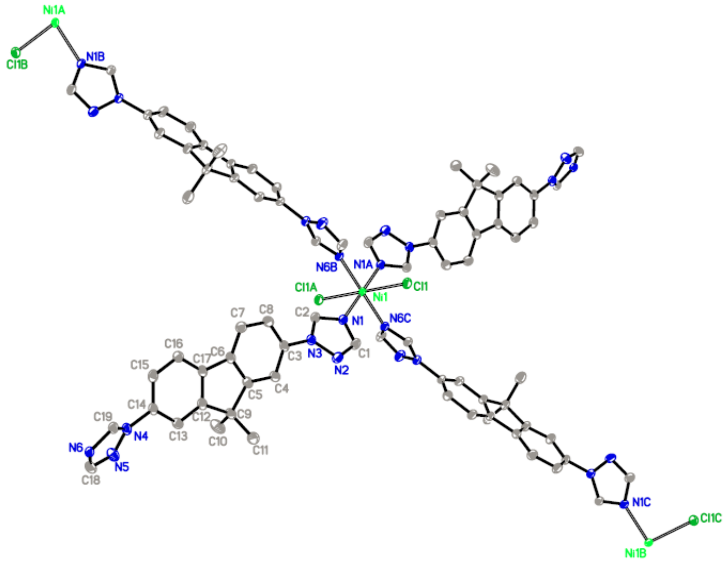


Fig. S5 The ORTEP figure of NiL_2Cl_2 (**2**).

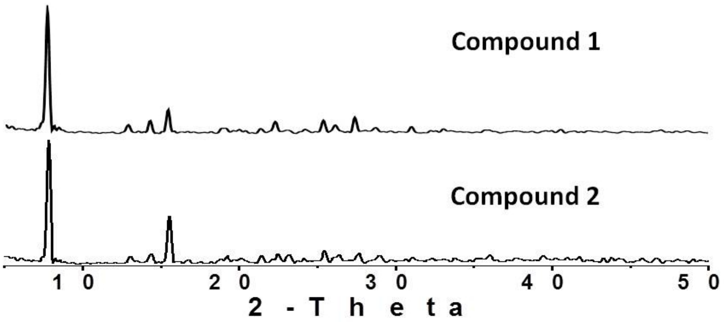


Fig. S6 XRPD patterns of **1** and **2**, indicating that the structure of **2** is identical to that of **1**.

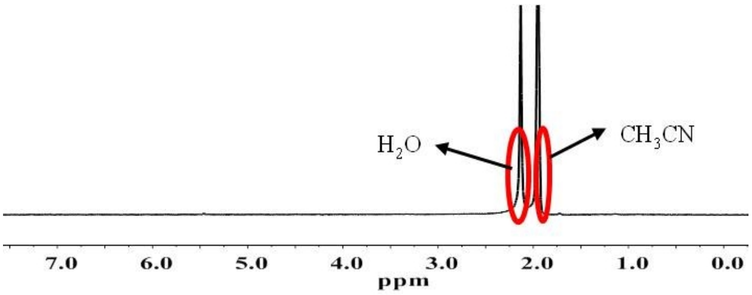


Fig. S7 ^1H NMR spectrum of the CD_3CN extract of **2**.

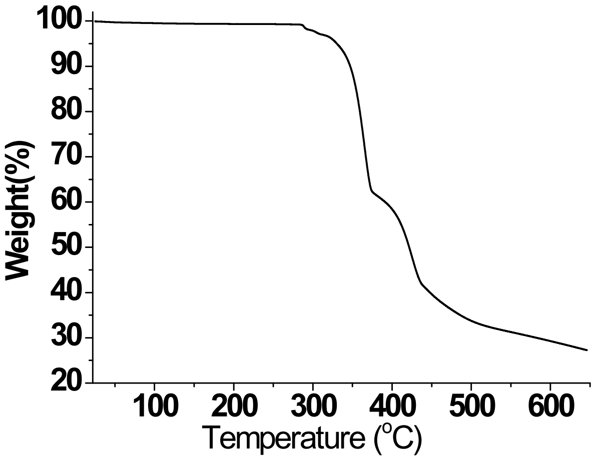


Fig. S8 TGA trace of **2**. No solvent mass loss was found which is well consistent with the single-crystal analysis result.

III. Compound 1′ (regenerated 1):

Synthesis of 1′: Compound **1** was suspended in the MeOH vapour in air for 24 h at ambient temperature, the MeOH and H_2O were taken inside to regenerate **1** (**1′**).

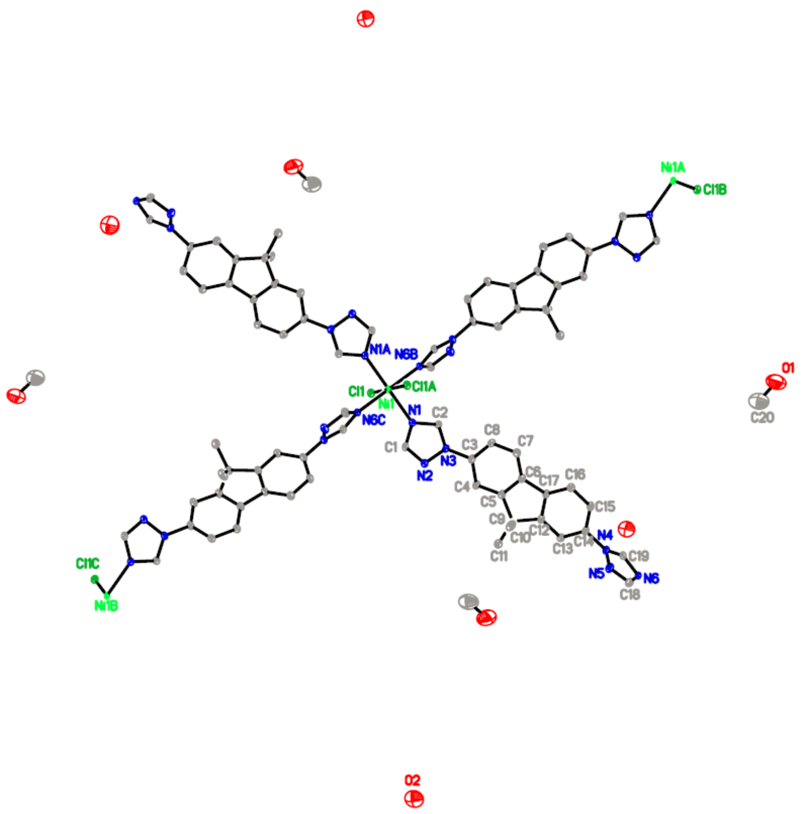


Fig. S9 The ORTEP figure of $NiL_2Cl_2 \cdot 2CH_3OH \cdot 0.5H_2O$ (**1'**).

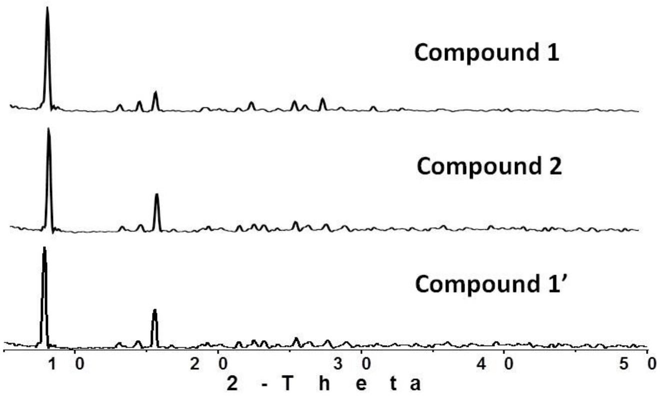


Fig. S10 XRPD patterns of **1**, **2** and regenerated of **1** (**1'**). The framework of Ni**L**$_2$Cl$_2$ is maintained during the reversible solvent adsorption process.

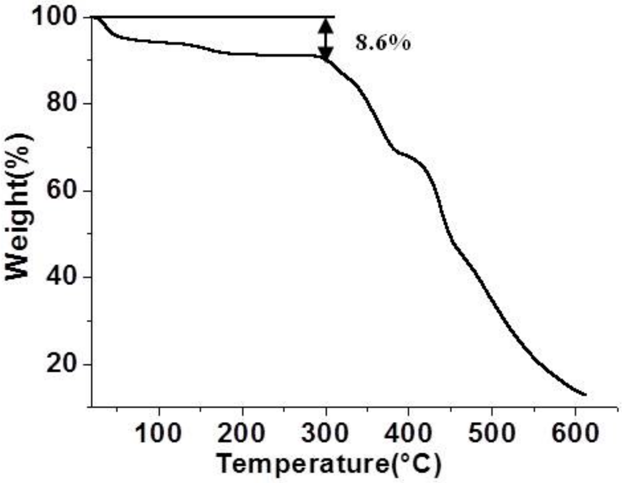


Fig. S11 TGA trace of **1’**. The observed solvent mass loss is 8.1 % (calculated 8.6%).

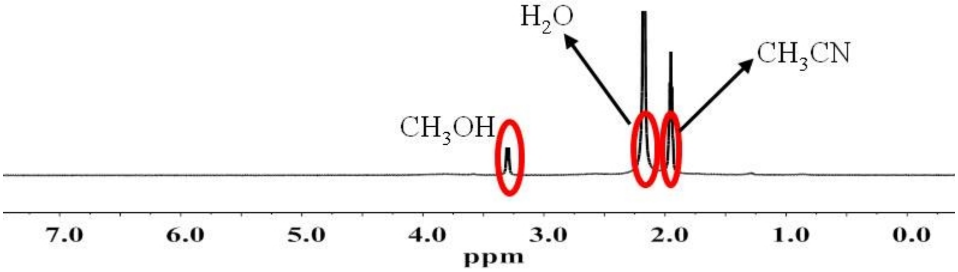


Fig. S12 ^{1}H NMR spectrum of the CD$_3$CN extract of **1’**.

IV. Compound 3

Synthesis of 3: The light blue crystals of **2** and some crystals of iodine were brought together in a closed system at ambient temperature ($p(I_2)$ is ca. 0.3 mm Hg) for 24 h to yield I_2-loaded compound **3**.

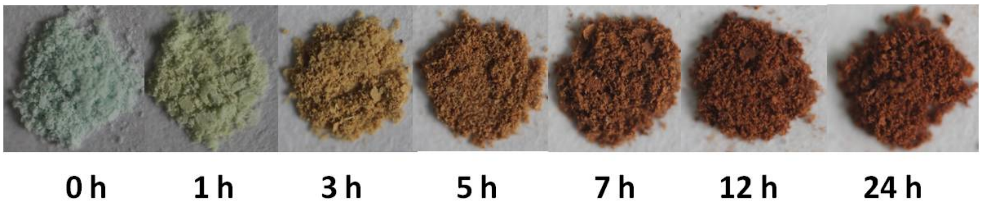


Fig. S13 Photographs showing the color change of the bulk samples of **2** in I_2 vapor at 0, 1, 3, 7, 12 and 24 h.

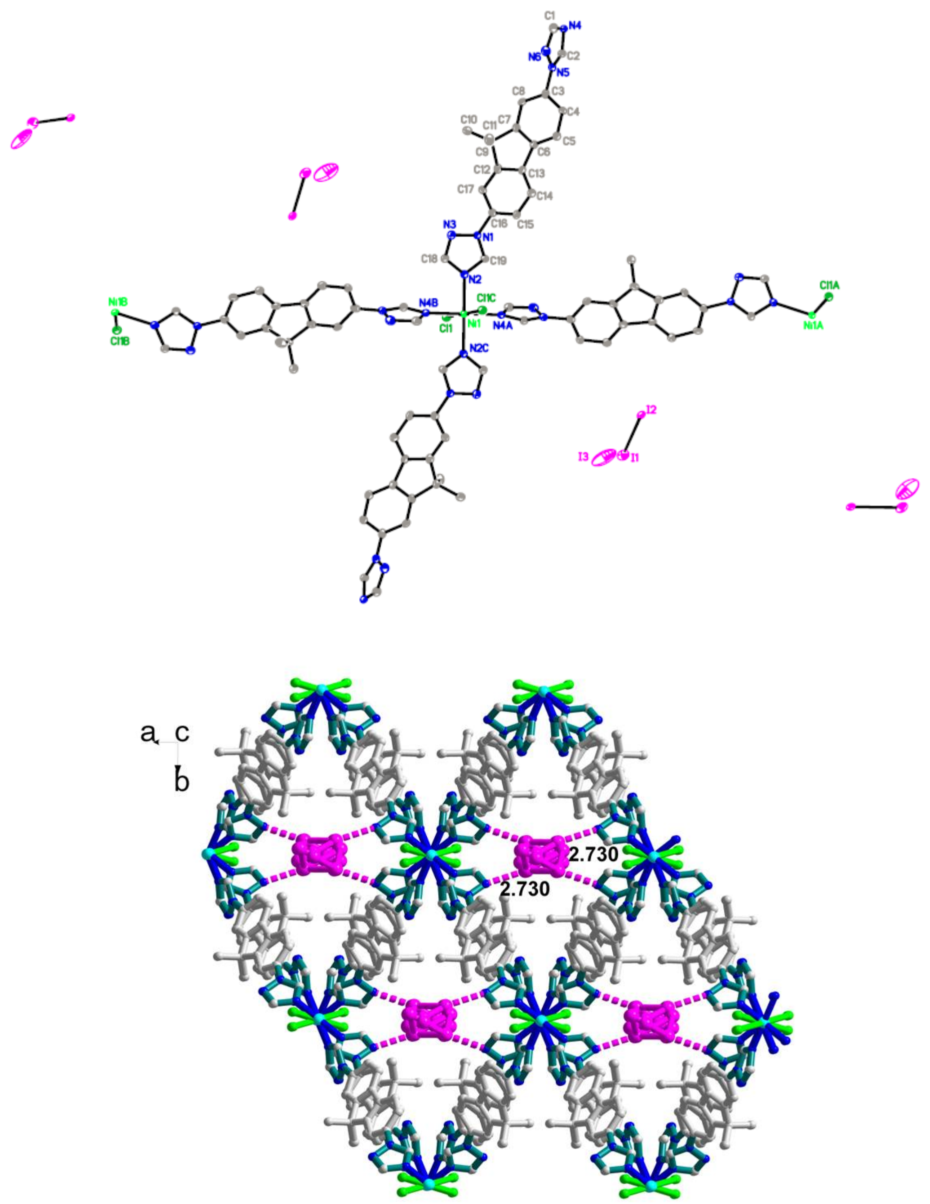


Fig. S14 Up: The ORTEP figure of $NiL_2Cl_2 \cdot 0.75I_2$ (**3**). Bottom: I_2 guest species is fixed by $I_2 \cdots N$ interaction.

V. Catalytic property

1. Catalytic reaction based on $0.75I_2 \subset NiL_2Cl_2$ (3)

Typical catalytic procedure: A mixture of benzaldehyde (1mmol), TMSCN (1.2mmol) and **3** (32.5mg, 0.033 mol) was stirred at ambient temperature (monitored by ^1H NMR) to afford the corresponding trimethylsilylated product of 2-phenyl-2-(trimethylsiloxy) acetonitrile. The product was purified by column chromatography on silica gel. ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS, ppm): $\delta = 0.24$ (s, 9H, –CH_3), 5.51(s, 1H, -CH), 7.41-7.48(m, 5H, -C_6H_5). When the reaction was finished, methylene chloride (1.5 mL) was added to the reaction system, **3** was recovered by centrifugation and filtration, and directly reused in the next run under the same conditions. The yield was determined by GC-MS.

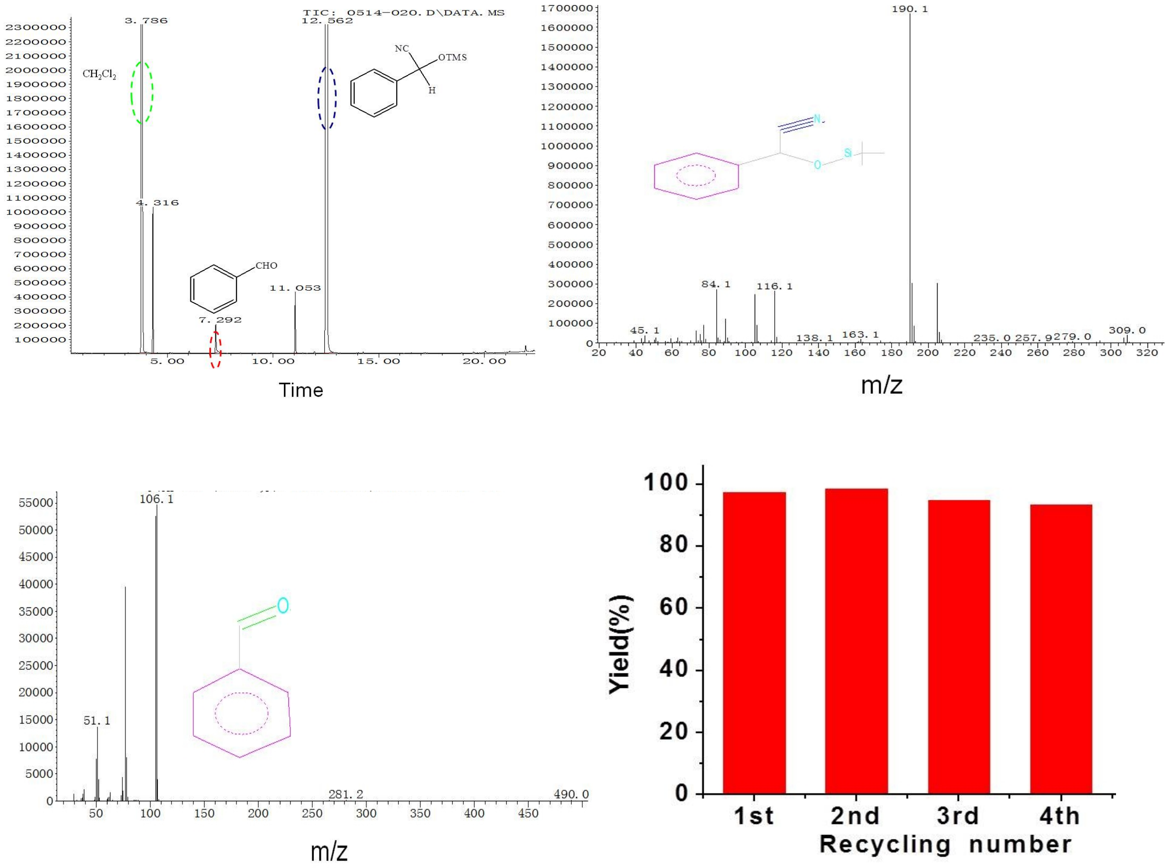
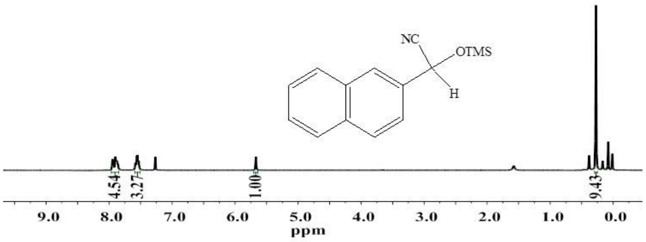
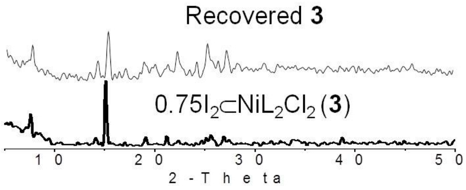


Fig. S 15 GC-MS spectra for the reaction for the second run (Yield, 98 %). The yields for the rest three runs are shown as bar chart (bottom right).

The catalytic cyanation reactions of 2-naphthaldehyde and 1-formylpyrene were carried out under the same reaction conditions. The yields for the corresponding trimethylsilylated products were determined by ^1H NMR spectra. 2-Naphthyl-2-(trimethylsiloxy) acetonitrile: ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS, ppm): δ = 0.27 (s, 9H, $-CH_3$), 5.67(s, 1H, -CH), 7.53-7.58(m, 3H, $-C_6H_3$), 7.88-7.95(m, 4H, $-C_6H_4$). 2-Pyrenyl-2-(trimethylsiloxy) acetonitrile: ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS, ppm): δ = 0.22 (s, 9H, $-CH_3$), 6.36(s, 1H, -CH), 8.05-8.16(m, 3H), 8.22-8.29(m, 5H), 8.41-8.44(d, J = 9Hz, 1H).





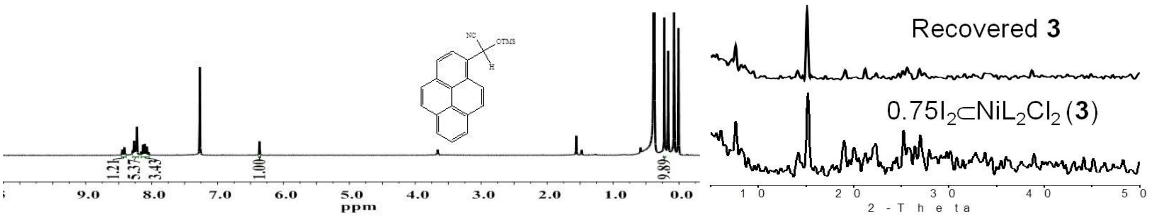


Fig. S16 Up: ^{1}H NMR spectrum directly performed on the reaction system, and no 2-naphthaldehyde substrate was found except the excess of TMSCN. XRPD patterns of **3** before and after the 2-naphthaldehyde cyanation reaction. Bottom: ^{1}H NMR spectrum directly performed on the reaction system, and no 1-formylpyrene substrate was found except the excess of TMSCN. XRPD patterns of **3** before and after the 1-formylpyrene cyanation reaction.

2. Catalytic reaction based on NiL$_2$Cl$_2$ (2)

Typical catalytic procedure: A mixture of benzaldehyde (1mmol), TMSCN (1.2mmol) and **2** (0.033 mol) was stirred at ambient temperature (monitored by ^{1}H NMR) to afford the corresponding trimethylsilylated product of 2-phenyl-2-(trimethylsiloxy) acetonitrile. The product was purified by column chromatography on silica gel. The yield was determined by GC-MS.

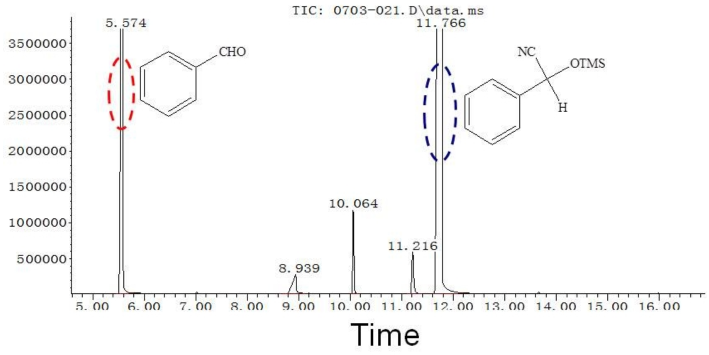
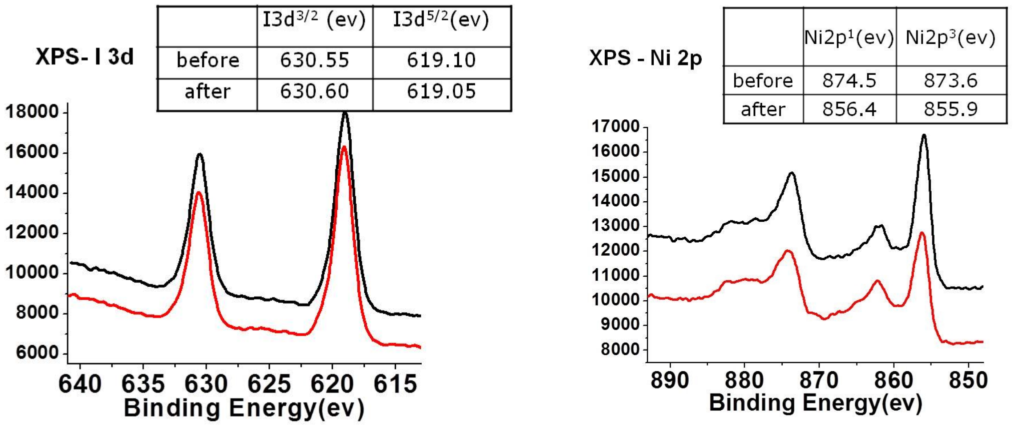


Fig. S 17 GC-MS spectrum for the reaction catalyzed by **2** (Yield, 76 %).



	I3d$^{3/2}$ (ev)	I3d$^{5/2}$(ev)
before	630.55	619.10
after	630.60	619.05

	Ni2p^1(ev)	Ni2p^3(ev)
before	874.5	873.6
after	856.4	855.9

Fig. S 18 The X-ray photoelectron spectroscopy (XPS) measurements performed on **3** before (red line) and after (black line) the reactions.

VI. Single-Crystal Structure Determination.

Suitable single crystals of **1**, **2**, **1’** and **3** were selected and mounted in air onto thin glass fibers. X-ray intensity data of these crystals were measured at 173(2) – 298 (2) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.71073 Å). The raw frame data were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[1] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[1] The crystal showed no evidence of crystal decay during data collection. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least squares technique. Crystal data, data collection parameters, and refinement statistics are listed in Tables S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 1027707-1027710. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for **1**, **2**, **1’** and **3**.

Compound	**1**	**2**	**1'**	**3**
Empirical formula	$C_{40}H_{41}Cl_2N_{12}NiO_{2.50}$	$C_{38}H_{32}Cl_2N_{12}Ni$	$C_{40}H_{41}Cl_2N_{12}NiO_{2.50}$	$C_{38}H_{32}Cl_2I_{1.50}N_{12}Ni$
Fw	859.46	786.37	859.46	976.72
Cryst syst	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
a (Å)	17.941(13)	18.101(14)	17.979(12)	18.421(13)
b (Å)	21.240(15)	20.893(16)	21.364(14)	20.910(14)
c (Å)	13.616(10)	13.626(11)	13.657(9)	13.545(10)
α (°)	90	90	90	90
β (°)	130.316(7)	130.367(8)	130.835(7)	130.190(9)
γ (°)	90	90	90	90

V (Å^3)	3956(5)	3926(5)	3969(5)	3986(5)
Space Group	*C2/c*	*C2/c*	*C2/c*	*C2/c*
Z value	4	4	4	4
$\rho calc.$(g/cm^3)	1.443	1.330	1.438	1.628
u(Mo Kα)(mm^{-1})	0.680	0.674	0.678	1.828
temp(K)	298(2)	298(2)	173(2)	173(2)
F(000)	1788	1624	1788	1942
Data / restraints / parameters	3720 / 32 / 275	3686 / 0 / 243	3732 / 2 / 282	3719 / 0 / 270
GOF on F^2	1.027	1.066	0.999	1.128
final R indices [I > 2sigma(I)]	*R1* = 0.0473 *wR2* = 0.1153	*R1* = 0.0432 *wR2* = 0.1211	*R1* =0.0425 *wR2* = 0.0984	*R1* =0.0837 *wR2* = 0.2105

Reference

(1) Sheldrick, G. M. SHELXTL Version 5.12; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 1997.