

Supporting Information

Incorporation of Ir(C^N)₂(N^N)-NiCl₂ in (N^N)-Covalent Organic Framework for Transcendent Dual Catalysis in Photochemical Cross-Coupling Synthesis

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1. General Information

1.1 Materials

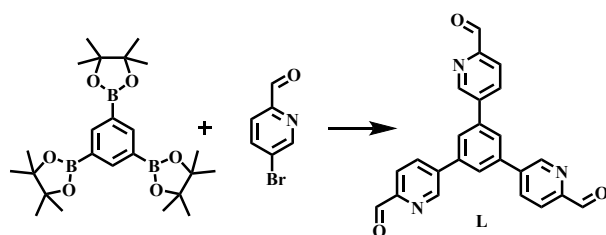
All the chemicals and solvents were purchased from commercially available sources (Sigma Aldrich GmbH, Bide Pharmatech Ltd, Energy Chemical and TCI Deutschland) and were used as received without further purification except otherwise noted.

1.2 General Procedures

Fourier-transform infrared (FT-IR) spectra (KBr pellets) were recorded on a Smart Omni-Transmission spectrometer in the of range 4000-400 cm^{-1} . Brunauer-Emmett-Teller (BET) surface areas were measured by N_2 adsorption and desorption at 77 K using a Micromeritics ASAP2020 analyzer. Pore size distribution was calculated from the adsorption or desorption branch with the nonlocal density functional theory (NLDFT). TGA was performed on a Mettler Toledo TGA/DSC 1000 analyzer under N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. PXRD spectra were measured by Bruker D8 Advance XRD diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54056\text{\AA}$). UV/Vis absorption spectra were recorded on a UV-2600 220V CH spectrometer (Shimadzu, Japan). ^1H NMR data was obtained using Bruker Avance IIIHD 400 MHz. ^{13}C NMR data was obtained using Bruker Avance IIIHD 700 MHz. Field emission SEM images, mapping images and energy dispersive x-ray spectrometry (EDS) was observed by JOEL JSM-7500FFSEM microscope. X-ray photoelectron spectroscopy XPS was performed on Kratos Axis Ultra DLD with monochromated $\text{Al K}\alpha$ radiation ($h\nu=1486.6\text{eV}$). The electrochemical test was performed on a CHI 760E electrochemical workstation. Photocatalytic reactions are carried out using a multi-channel photochemical reaction system featuring 10W 450nm LED lamps. The reaction of oxidation was monitored by GC (GC-14C, Shimadzu) equipped with a HP-5 column, air carrier gas and FID conductivity detector. The product was further confirmed with gas chromatography-mass spectrometer (GC-MS) Agilent 7890A/5975C.

2. Synthesis of materials

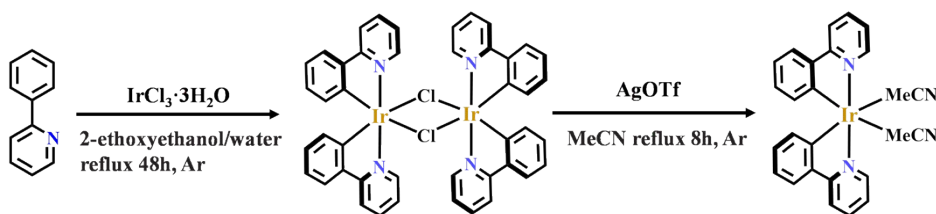
2.1 Synthesis of 5,5',5''-(benzene-1,3,5-triyl)tripicolinaldehyde (L)



L were synthesized as per literature procedures¹. A mixture of 1,3,5-tris(4,4,5,5-tetramethyl-

1,3,2-dioxaborolan-2-yl)benzene (680 mg, 1.5 mmol), 5-bromo-2-pyridinecarboxaldehyde (1.25 mg, 6.7 mmol), K_2CO_3 (3 g, 22 mmol), $Pd(PPh_3)_4$ (516.9 mg, 0.44 mmol) in anhydrous DMF (100 mL) was degassed and stirred under N_2 atmosphere at 90 °C for 24h. The solvent was removed under reduced pressure and the solid residue triturated with water, collected by filtration and washed with water (3×), hot diethyl ether (2×) and hot hexane (2×). The dried solid was triturated with CH_2Cl_2 and collected again. The resulting product was redissolved in hot $CHCl_3$, the insoluble materials filtered off and Et_2O added to the filtrate to precipitate out pure product as a pale yellow solid (230 mg, 40%). 1H NMR ($CDCl_3$, 400 MHz): δ = 10.17 (s, 1H), 9.12 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.95 (s, 1H); ^{13}C ($CDCl_3$, 700 MHz): δ = 192.8, 152.3, 148.7, 139.30, 139.28, 135.6, 127.0, 121.9. ESI-MS: m/z 393.1 ($[M + H]^+$)

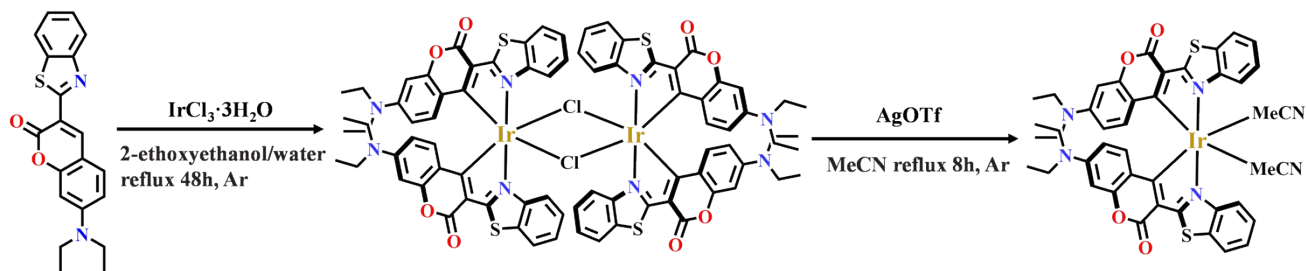
2.2 Synthesis of $[Ir(ppy)_2Cl]_2$ (ppy = 2-phenylpyridine, OTf = trifluoromethanesulfonic)



$[Ir(ppy)_2Cl]_2$ were synthesized as per literature procedures². $IrCl_3 \cdot 3H_2O$ (194.0mg, 0.55mmol) and 2-phenylpyridine (190.0mg, 1.22mmol) were dissolved in a mixture of 2-ethoxyethanol (30mL) and water (10mL), which was refluxed for 24h under an argon atmosphere. Then the solution was cooled to room temperature, the resulting yellow precipitate was collected with a glass filter frit. The precipitate was successively washed with ethanol (30mL) and acetone (30mL) to obtain the yellow solid $[Ir(ppy)_2Cl]_2$ with a yield of 91.0% (270.5mg). 1H NMR (500 MHz, $C_2D_2Cl_4$): 9.17 (4H, d, J = 6.9 Hz, H_A), 7.90 (4H, d, J = 7.7 Hz, H_D), 7.79 (4H, m, H_C), 7.55 (4H, d, J = 6.9 Hz, H_E), 6.86 (4H, m, H_F), 6.81 (4H, m, H_B), 6.65 (4H, m, H_G), 5.95 (4H, d, J = 7.7 Hz, H_H); ^{13}C NMR (700 MHz, $C_2D_2Cl_4$): 168.0, 151.3, 144.5, 144.0, 136.5, 130.5, 129.1, 123.7, 122.3, 121.5, 118.4.

$[Ir(ppy)_2Cl]_2$ (107.2, 0.1mmol), $AgOTf$ (OTf = triflate) (51.4mg, 0.2mmol) and 10mL acetonitrile were taken in a 100 mL Schlenk tube. The tube was immersed in a preheated oil bath at 80 °C and stirred for 8 h under an argon atmosphere in a dark environment. Then, the tube was removed from the oil bath and allowed to cool to room temperature. The white precipitate formed during the reaction was filtered off, and the yellow filtrate $[Ir(ppy)_2(MeCN)_2]OTf$ in acetonitrile was collected in a 25mL Schlenk tube, and the tube was stored under nitrogen protection. The concentration of $[Ir(ppy)_2(MeCN)_2]OTf$ was 0.02mmol/mL.

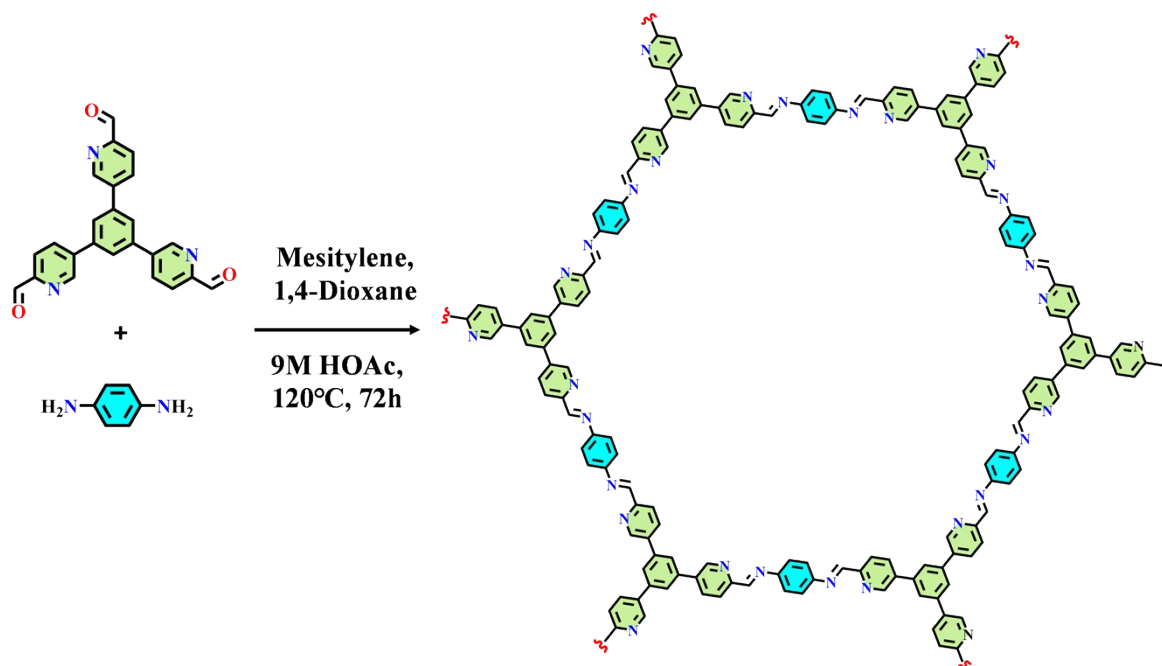
2.3 [Ir(coum)₂Cl]₂ (coum = 3-(2-Benzothiazolyl)-7-(diethylamino)coumarin)



IrCl₃·3H₂O (194.0mg, 0.55 mmol) and Coumarin 6 (430.0mg, 1.22mmol) were dissolved in a mixture of 2-ethoxyethanol (30mL) and water (10mL), which was refluxed for 24 h under an argon atmosphere. Then, the solution was cooled to room temperature, and the yellow precipitate was collected with a glass filter frit. The precipitate was washed with ethanol (30mL) and acetone (30mL) to obtain the orange solid [Ir(coum)₂Cl]₂ with a yield of 84.9 % (433.2mg). ¹H NMR (CDCl₃, 400 MHz): δ = 7.89 (d, 1H), 7.33 (d, 1H), 7.06 (m, 2H), 6.14 (s, 1H), 5.31 (d, 1H), 4.99 (d, 1H), 3.09 (m, 4H), 0.91 (t, 6H).

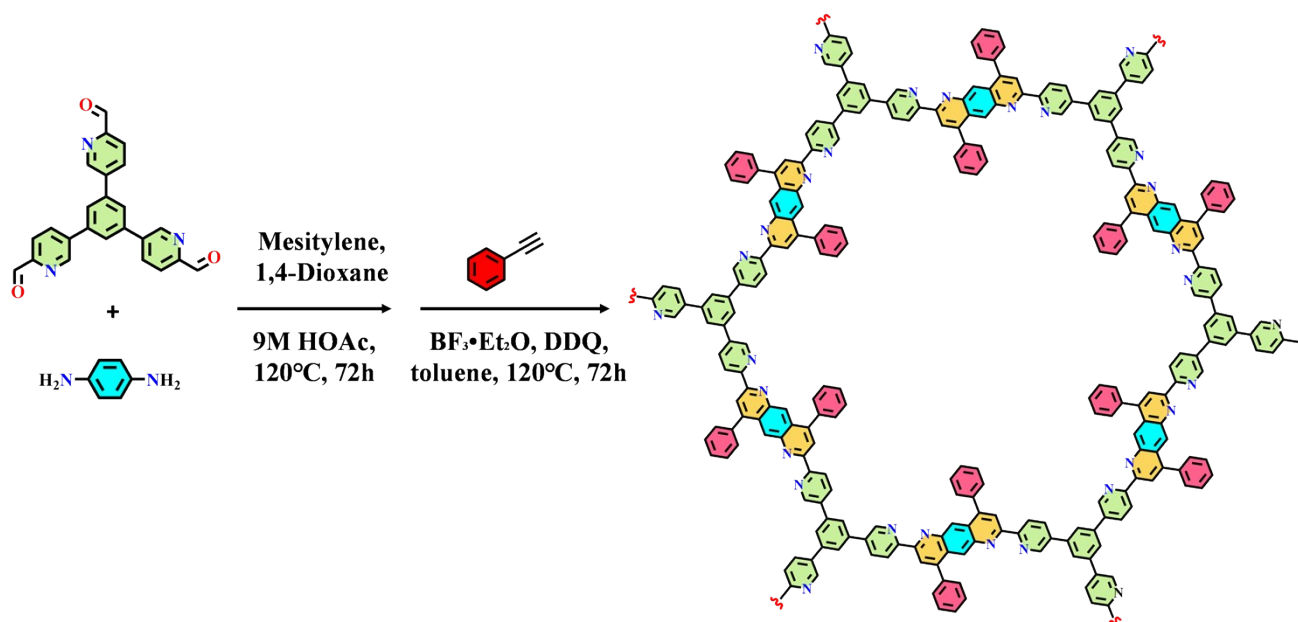
[Ir(coum)₂Cl]₂ (185.2mg, 0.1mmol), AgOTf (OTf = triflate) (51.4mg, 0.2mmol) and 10mL acetonitrile were taken in a 100 mL Schlenk tube. The tube was immersed in a preheated oil bath at 80 °C and stirred for 8 h under an argon atmosphere in a dark environment. Then, the tube was removed from the oil bath and allowed to cool to room temperature. The white precipitate formed during the reaction was filtered off, and the yellow filtrate [Ir(coum)₂(MeCN)₂]OTf in acetonitrile was collected in a 25mL Schlenk tube, and the tube was stored under nitrogen protection. The concentration of [Ir(coum)₂(MeCN)₂]OTf was 0.02mmol/mL.

2.4 Synthesis of I-COF



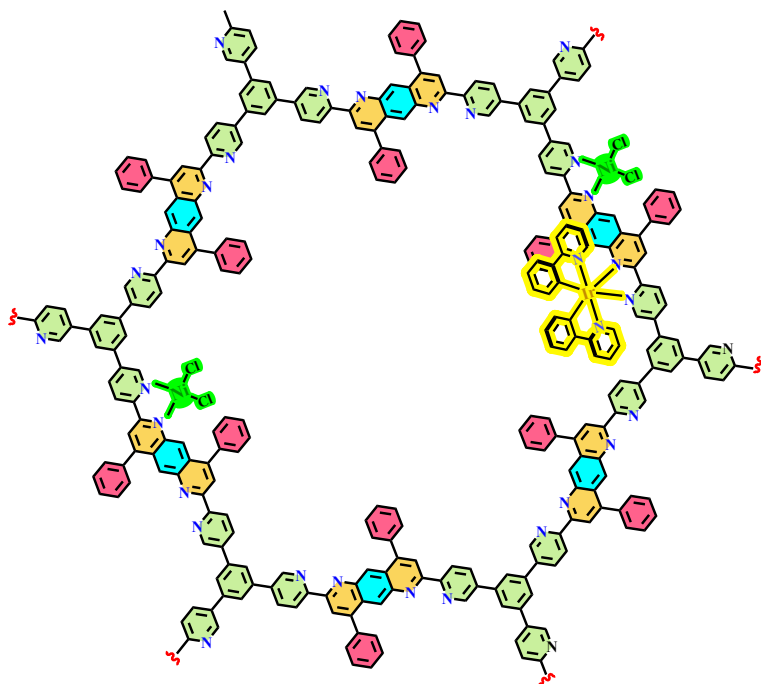
A Pyrex tube measuring 10×8 mm (o.d × i.d) was charged with **L** (15.72mg, 0.04mmol), benzene-1,4-diamine (6.48mg, 0.06mmol), 0.8mL of a mixture of 0.2 mL mesitylene and 0.6 mL 1,4-Dioxane, 0.06 mL of 9M aqueous acetic acid water. The tube was flash frozen at 77 K (liquid N₂ bath), evacuated to an internal pressure of 150 mTorr and flame sealed. The reaction was heated at 120 °C for 72 h yielding a yellow solid at the bottom of the tube which was isolated either by filtration or centrifugation and washed with DMA and THF, the resulting powder was dried at 10⁻² mTorr under 100 °C for 12 h and to afford two-dimensional imine-based **I-COF** as a yellow solid.

2.5 Synthesis of Q-COF



A Pyrex tube measuring 10×8 mm (o.d × i.d) was charged with **L** (15.72mg, 0.04mmol), benzene-1,4-diamine (6.48mg, 0.06mmol), 0.8mL of a mixture of 0.2 mL mesitylene and 0.6 mL 1,4-Dioxane, 0.06 mL of 9M aqueous acetic acid water. The tube was flash frozen at 77 K (liquid N₂ bath), evacuated to an internal pressure of 150 mTorr and flame sealed. The reaction was heated at 120 °C for 72 h yielding a yellow solid at the bottom of the tube which was isolated either by filtration or centrifugation and washed with DMA and THF, the resulting powder was subsequently subjected to the reaction with phenylacetylene (12.24mg, 0.12mmol) at 120 °C in the presence of BF₃·Et₂O (16.00μL, 0.12mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (32.00mg, 0.12 mmol) in toluene for 72 h. The solid separated from the reaction mixture was washed with excess anhydrous THF and saturated NaHCO₃, and then dried under vacuum to afford quinoline-linked **Q-COF** as dark yellow solid. Yield: 29.02mg, 90% based on **L**.

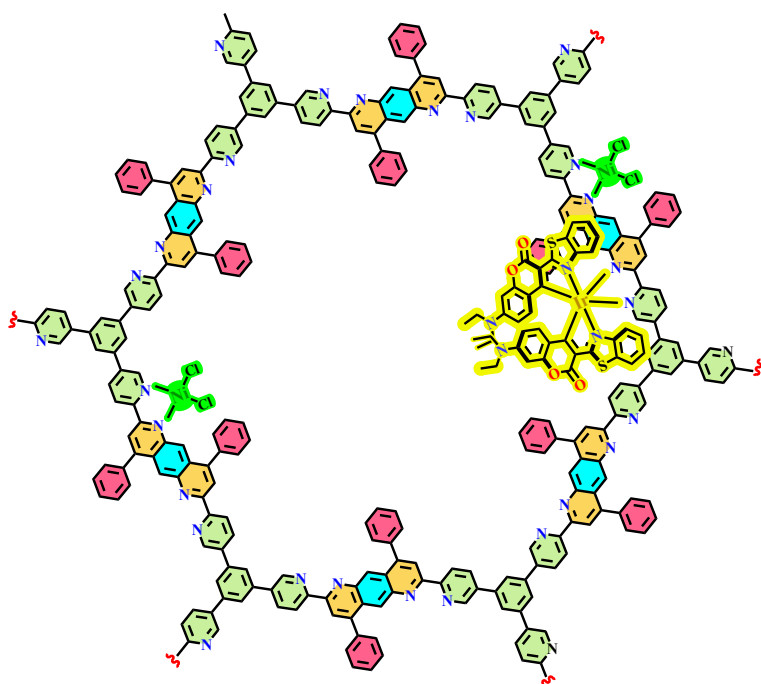
2.6 Synthesis of $[\text{Ir}(\text{ppy})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$



In a 25 mL round bottom-flask, 20.0 mg of **Q-COF** were suspended on 5 mL of acetonitrile. $[\text{Ir}(\text{ppy})_2(\text{MeCN})_2]\text{OTf}$ in acetonitrile (5% equiv. per $\text{N}^{\wedge}\text{N}$ functionality) was added. The mixture was stirred at 80°C for 12 hours. After heating, the tube was removed from the oil bath and allowed to cool to room temperature. The residue was washed with DMA and THF. The washing was repeated another two times.

Then, 5mL DMA and $\text{Ni}(\text{DME})\text{Cl}_2$, (10% equiv. per $\text{N}^{\wedge}\text{N}$ functionality) was added. The mixture was stirred at 60°C for 12 hours, yielding a brown powder that was isolated by filtration and washed with DMA and THF. The resulting powder was washed with THF using Soxhlet extraction, then filtered and dried first at room temperature under vacuum for 12 h, and then at 120 °C for 24 h to afford an reddish-brown powder, $[\text{Ir}(\text{ppy})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$.

2.7 Synthesis of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$



In a 25 mL round bottom-flask, 20.0 mg of **Q-COF** were suspended on 5 mL of acetonitrile. $[\text{Ir}(\text{coum})_2(\text{MeCN})_2]\text{OTf}$ in acetonitrile (5% equiv. per $\text{N}^{\wedge}\text{N}$ functionality) was added. The mixture was stirred at 80°C for 12 hours. After heating, the tube was removed from the oil bath and allowed to cool to room temperature. The residue was washed with DMA and THF. The washing was repeated another two times.

Then, 5mL DMA and $\text{Ni}(\text{DME})\text{Cl}_2$, (10% equiv. per $\text{N}^{\wedge}\text{N}$ functionality) was added. The mixture was stirred at 60°C for 12 hours, yielding a brown powder that was isolated by filtration and washed with DMA and THF. The resulting powder was washed with THF using Soxhlet extraction, then filtered and dried first at room temperature under vacuum for 12 h, and then at 120 °C for 24 h to afford an reddish-brown powder, $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$.

3. General procedure for photocatalytic process

3.1 $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ catalyzed C-S cross-coupling of thiophenols and aryl iodides

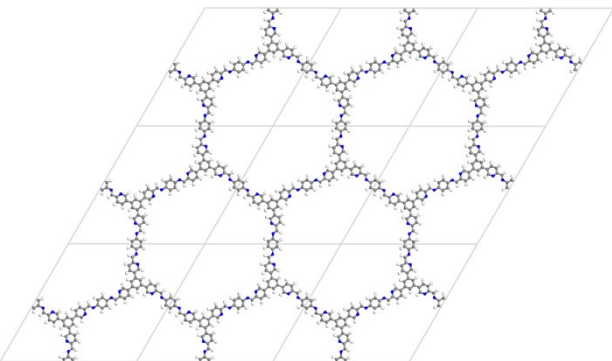

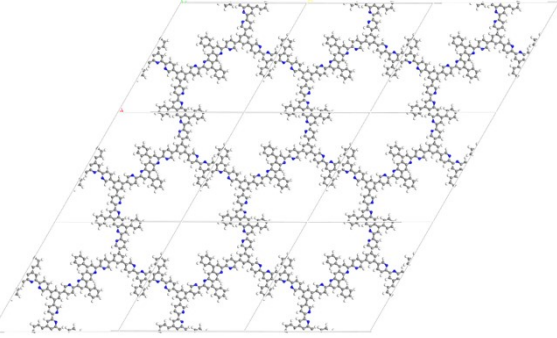

Under N_2 atmosphere, 2mg $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$, 0.2 mmol aryl iodide, 0.3 mmol thiophenol, 0.3 mmol pyridine, and 0.2 mL acetonitrile were added into a 10mL photocatalytic bottle, under irradiation of 10 W 450nm LED lamp for 12h at room temperature. Afterwards, the catalyst was removed from the reaction mixture via centrifugation and the solution was extracted with acetonitrile. Conversions were determined by gas chromatography.

3.2 [Ir(coum)₂(N[^]N)+NiCl₂]@Q-COF catalyzed C-N cross-coupling of amines and aryl iodides

Under N₂ atmosphere, 2mg [Ir(coum)₂(N[^]N)+NiCl₂]@Q-COF, 0.1mmol aryl iodide, 0.15 mmol amines, 0.15 mmol 1,1,3,3-tetramethylguanidine (TMG), and 0.1mL acetonitrile were added into a 10mL photocatalytic bottle, under irradiation of 10 W 450nm LED lamp for 24h at room temperature. Afterwards, the catalyst was removed from the reaction mixture via centrifugation and the solution was extracted with acetonitrile. Conversions were determined by gas chromatography.

4. Characterization analysis

Table S1. Unit cell parameters and structures of I-COF and Q-COF

Unit cell parameters	COF structures
I-COF with AA packing Space group: P6 a= b= 37.4999Å c= 3.4693 Å $\alpha = \beta = 90^\circ \gamma = 120^\circ$ R _{WP} = 4.39 % R _p = 2.87%	<p>Top view </p> <p>Side view </p>
Q-COF with AA packing Space group: P6 a= b= 36.8486Å c= 3.4993 Å $\alpha = \beta = 90^\circ \gamma = 120^\circ$ R _{WP} = 5.58 % R _p = 3.95%	<p>Top view </p> <p>Side view </p>

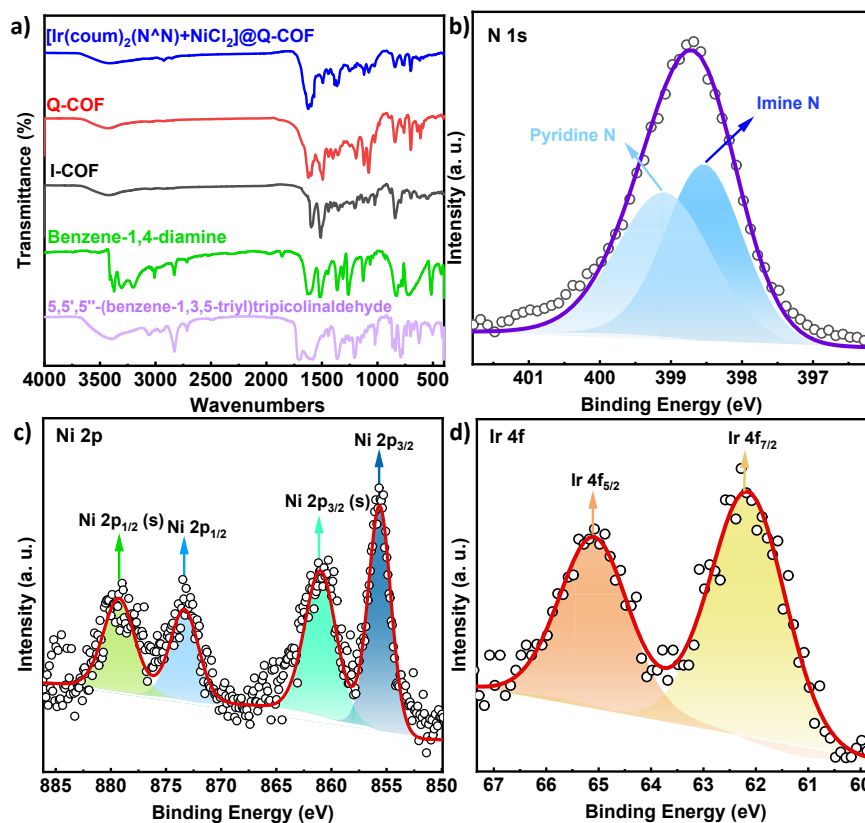


Figure S1 a) FT-IR spectra of reactants, I-COF, Q-COF and $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$, b) N 1s XPS patterns of I-COF, c) Ni 2p and d) Ir 4f XPS patterns of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$.

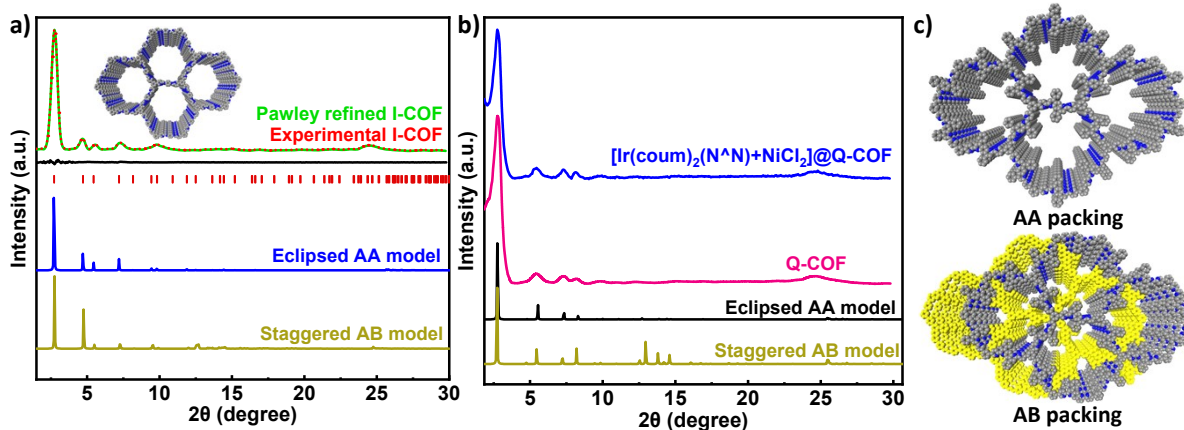


Figure S2 a) The simulated, experimental and Pawley refined PXRD patterns of I-COF. b) PXRD patterns of Q-COF and $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$. c) AA and AB packing structures of Q-COF

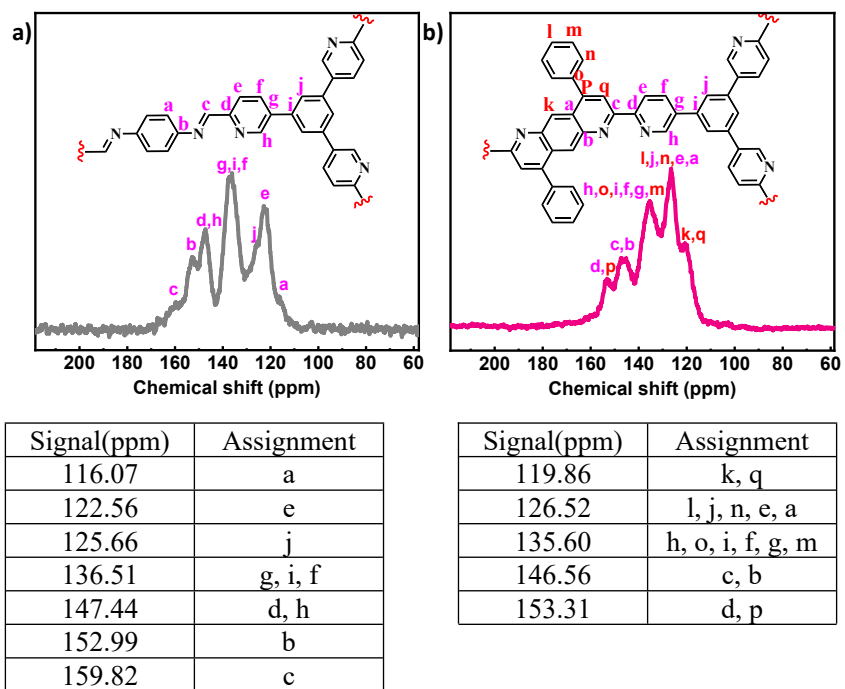


Figure S3 Solid-state ^{13}C NMR spectroscopy of a) I-COF and b) Q-COF

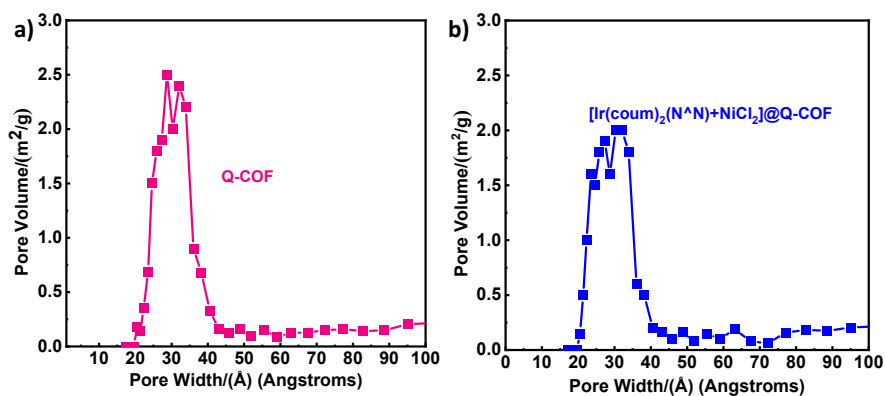


Figure S4 Pore size distribution of a) Q-COF and b) $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$

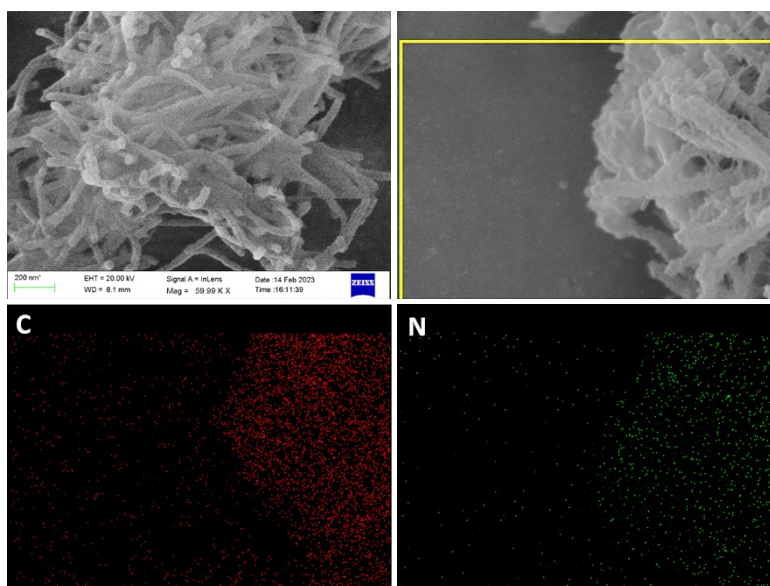


Figure S5 SEM and EDS mapping image of Q-COF

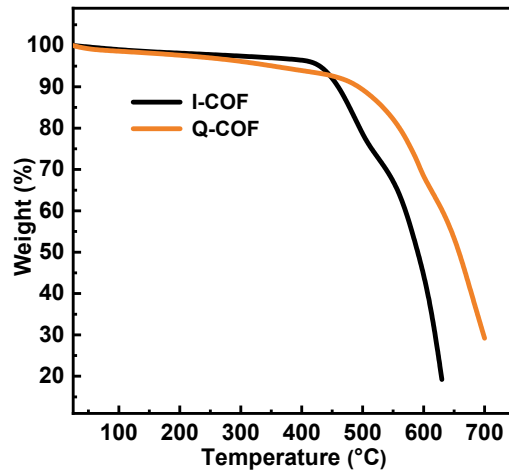


Figure S6 TGA curves of the I-COF and Q-COF under air atmosphere

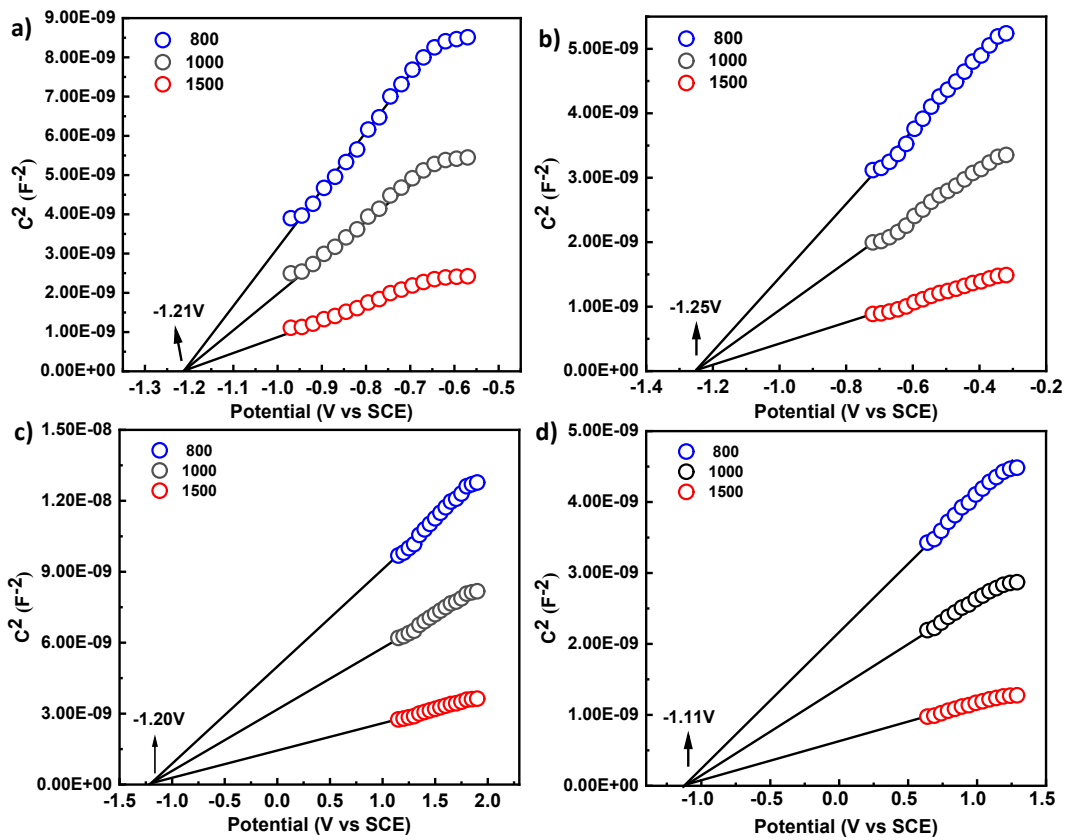


Figure S7 Mott-Schottky plots of a) I-COF, b) Q-COF, c) $[\text{Ir}(\text{ppy})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ and d) $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$

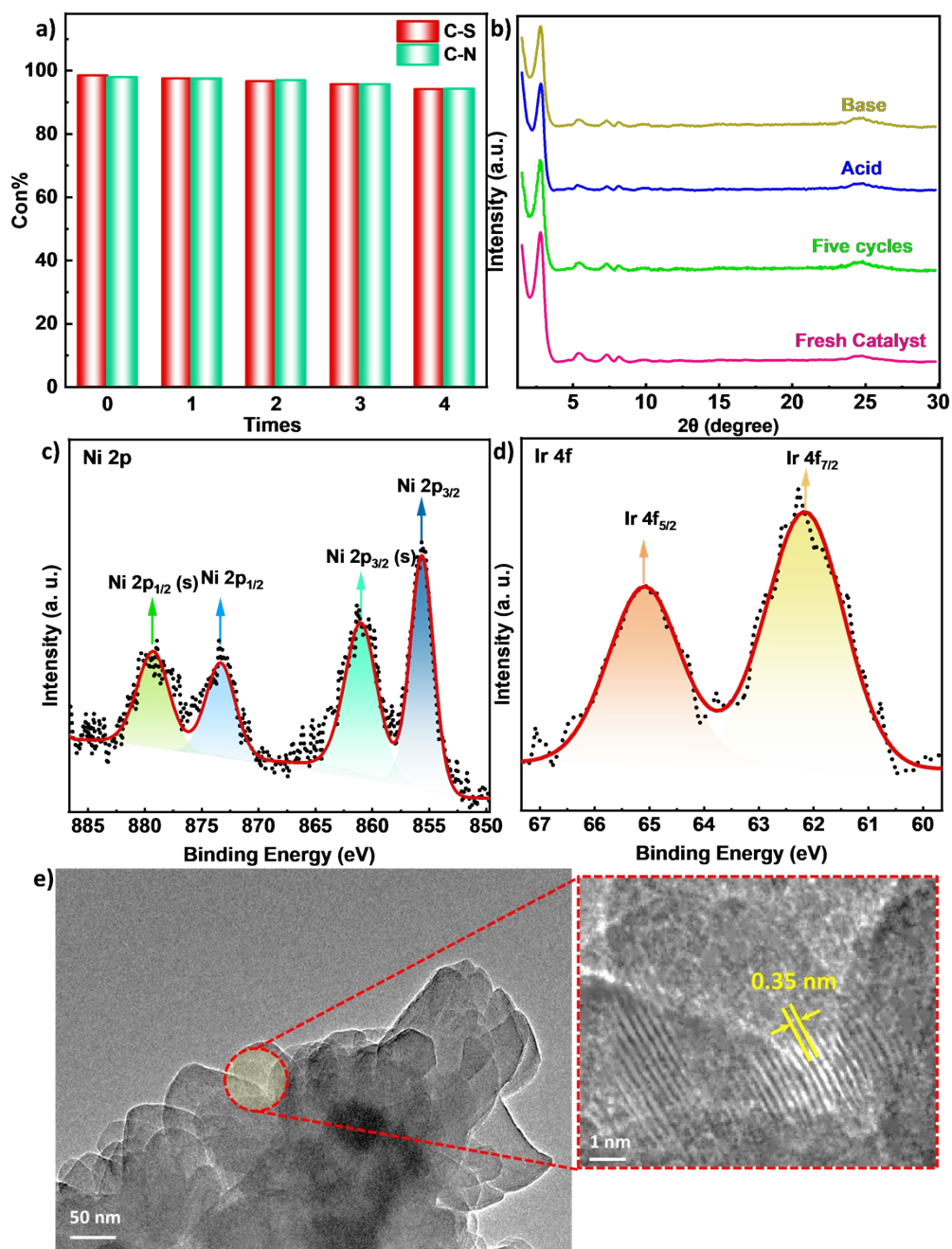


Figure S8 a) The recyclability and b) PXRD patterns of of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ for stability studies. c) Ni 2p and d) Ir 4f XPS patterns of recycled $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$. e) TEM of recycled $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$

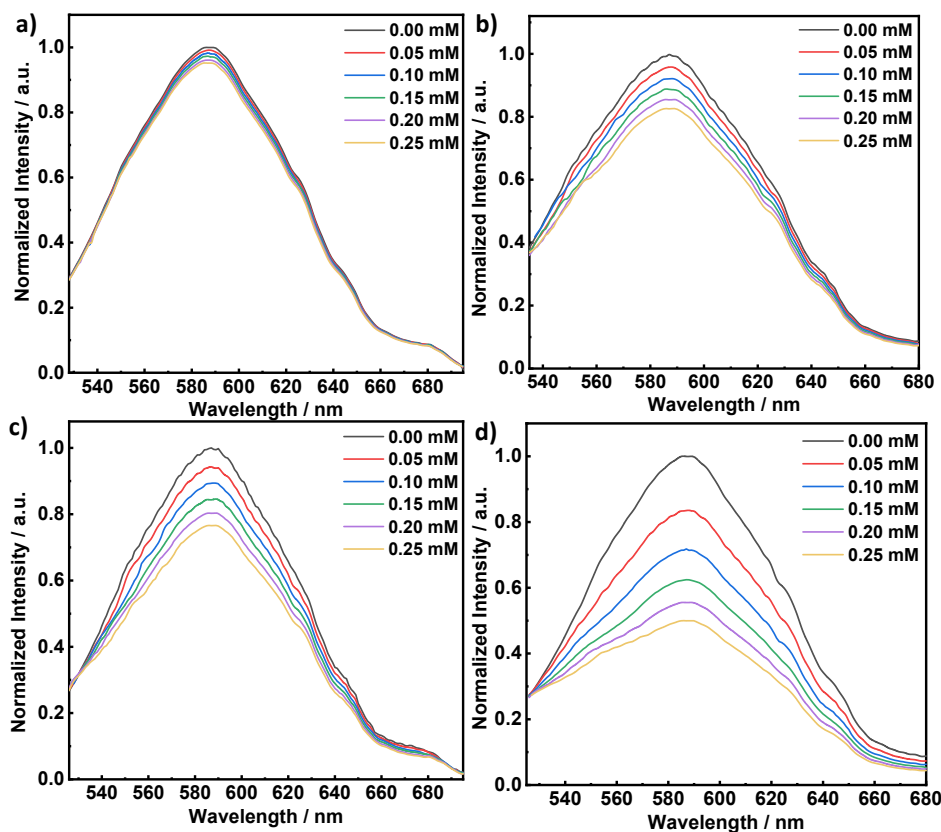


Figure S9 Emission spectra of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ (0.02 mM, MeCN) after the addition of different amounts of **a)** 1-iodo-4-(trifluoromethyl)benzene, **b)** 4-methylbenzenethiol, **c)** Pyridine, and **d)** 4-methylbenzenethiol+pyridine (based on the reaction ratio) with 450 nm excitation.

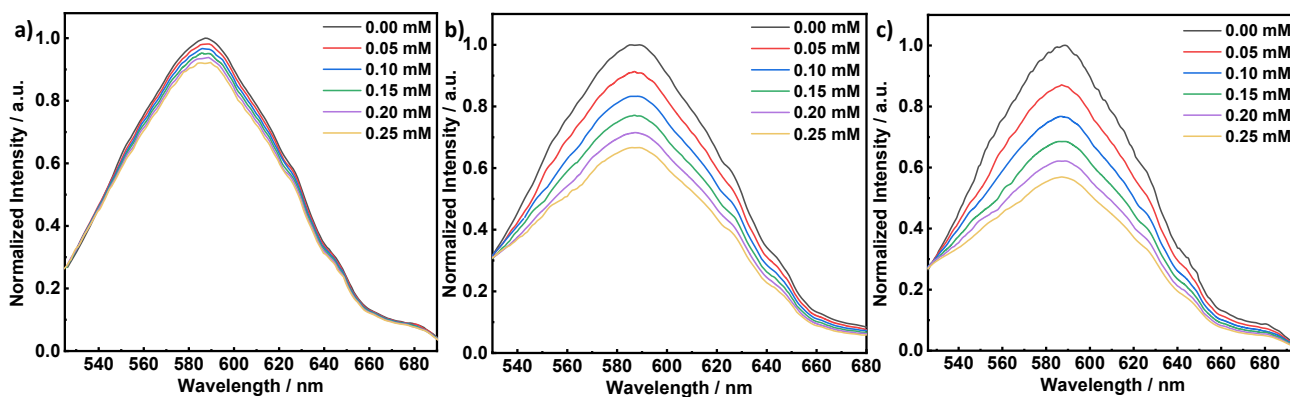


Figure S10 Emission spectra of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ (0.02mM, MeCN) after the addition of different amounts of **a)** Aniline, **b)** 1,1,3,3-tetramethylguanidine(TMG), and **c)** aniline+TMG (based on the reaction ratio) with 450 nm excitation.

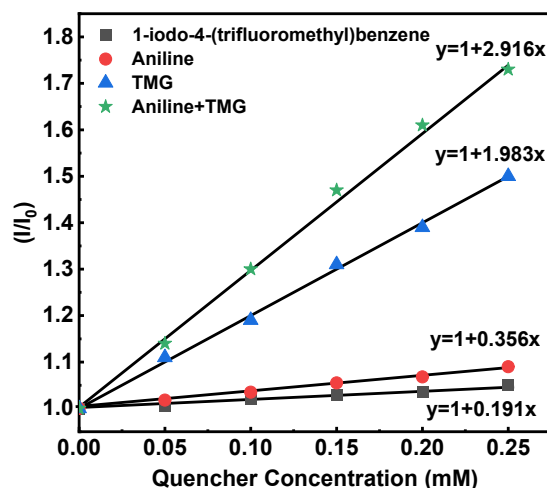


Figure S11 Comparative Stern-Volmer quenching plot during C-N cross coupling reactions.

$$\text{Stern-Volmer equation } (I_0/I) = 1 + K_{sv}[Q];$$

where (I_0/I) = The ratio of fluorescence intensity in the absence and the presence of quencher,

K_{sv} = quenching constant,

$[Q]$ = quencher concentration,

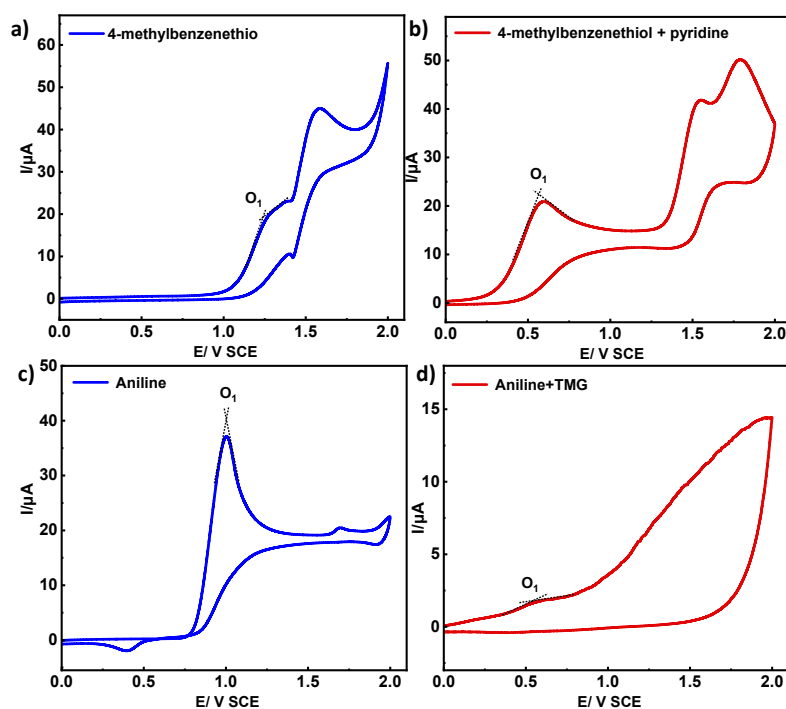


Figure S12 Cyclic voltammograms of reactants **a)** 4-methylbenzenethiol, **b)** 4-methylbenzenethiol + pyridine, **c)** Aniline, **d)** Aniline+TMG (based on the reaction ratio) with 0.1 M TBAH (tetrabutylammonium hexafluorophosphate) in acetonitrile solution under N_2 with scan rate of 100 mV/s. Conditions: 1 mM, a negative scan direction. Glassy carbon working electrode, saturated calomel electrode (SCE) reference electrode, and Pt silk counter electrode.

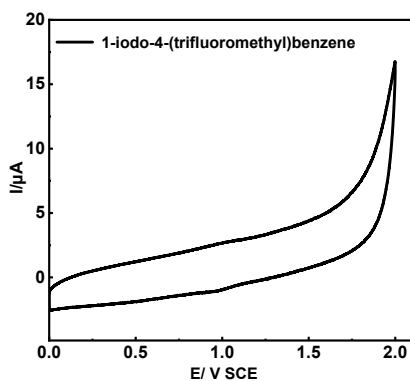


Figure S13 Cyclic voltammograms of reactant 1-iodo-4-(trifluoromethyl)benzene

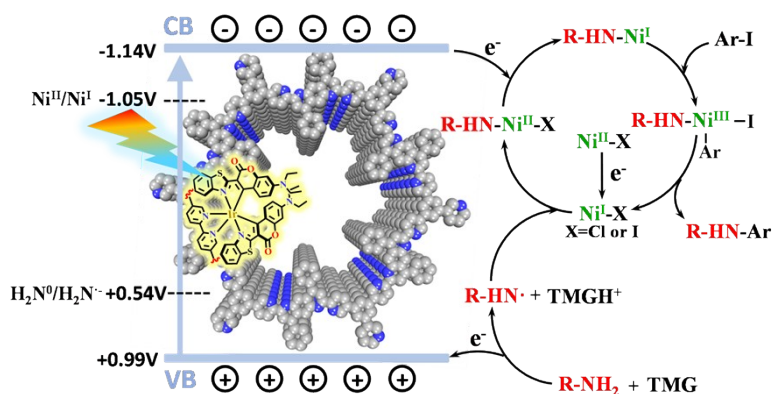


Figure S14 Proposed mechanisms of $[\text{Ir}(\text{coum})_2(\text{N}^{\wedge}\text{N})+\text{NiCl}_2]@\text{Q-COF}$ catalyzed C-N cross-coupling of amines and aryl iodides

5 Computational Studies methods for binding energy

The binding energy ΔE of π - π interaction between reactants or products with dangling phenyl moieties in COF was carried out by Forced Calculation, which was widely used in molecular mechanics on Material studio 2020.

The **Q-COF** was constructed with reactants closed to the dangling phenyl moieties. Task was on geometry optimization, Forcefield on COMPASSII, and Charges on Use current. The geometry optimized position of reactants and products in **Q-COF** was shown in Figure S13. Then, the same computing method but for Task on Energy was carried out for $E_{(A)}$, $E_{(B)}$ and $E_{(AB)}$, respectively. $E_{(A)}$ stands for the total energy of reactants and products, $E_{(B)}$ for **Q-COF**, $E_{(AB)}$ for reactants and products in **Q-COF**. Finally, the binding energy ΔE of π - π interaction was calculated by the Eq. S3, as shown in **Table S1**.

$$\Delta E = E_{(AB)} - E_{(A)} - E_{(B)} \text{ (Eq. S3)}$$

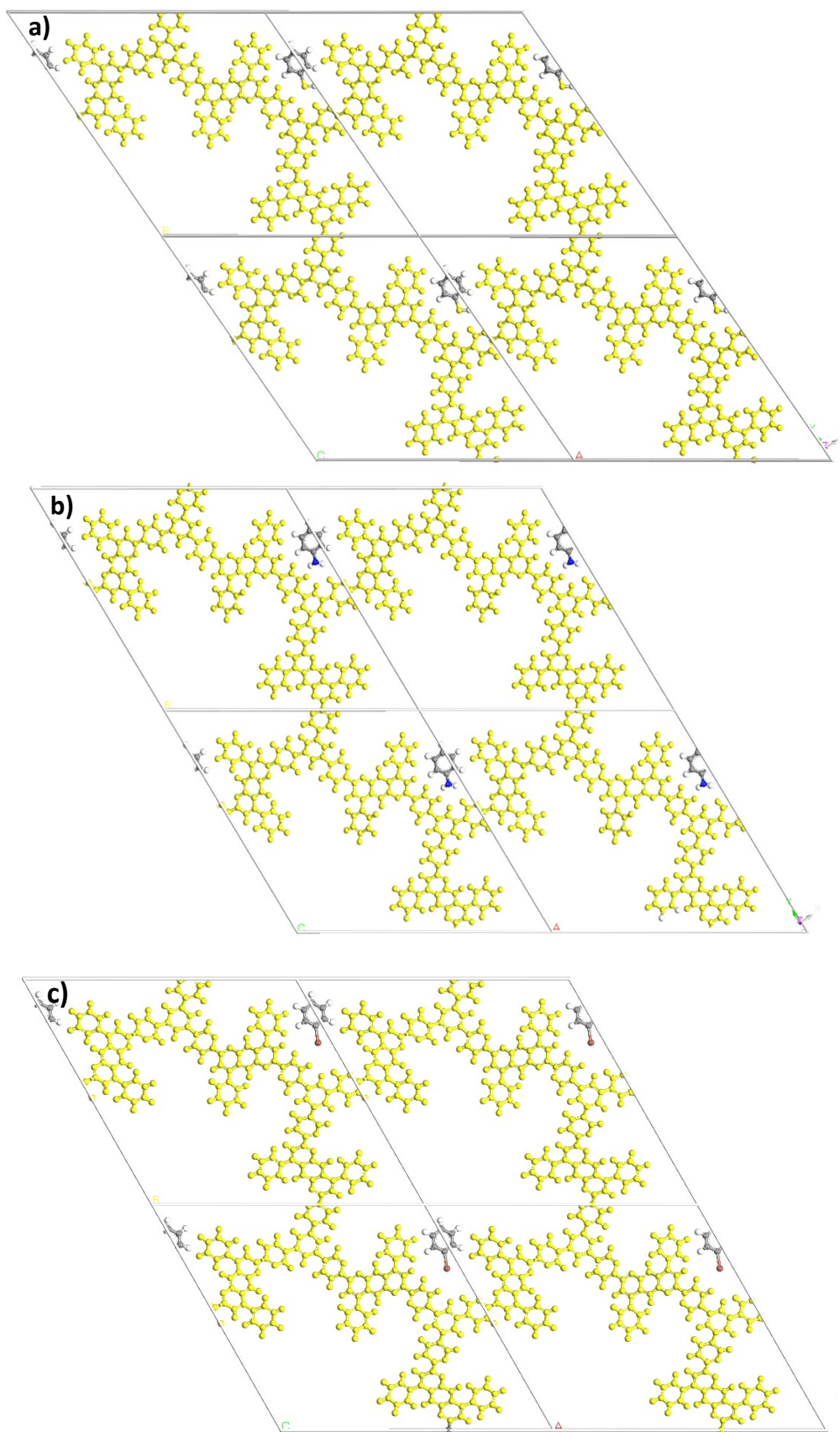


Figure S15. The geometry and energy optimized diagram of reactants and COF: **a)** Benzenethiol, **b)** Aniline, **c)** Iodobenzene

Table S2. The binding energy between substrates with dangling phenyl moieties in the pores of COF

Compounds	Total energy $\Delta E/\text{kcal/mol}$
Benzenethiol	-13.5575
Aniline	-11.7035
Iodobenzene	-11.6977

Table S3. Fractional atomic coordinates for the unit cell of **I-COF**

Element	Atom Number	<i>x</i>	<i>y</i>	<i>z</i>
H	1	0.715716	0.305078	0
H	2	0.773329	0.342434	0
H	3	0.829661	0.496532	0
H	4	0.751901	0.447861	0
H	5	0.606308	0.098466	0
H	6	0.578175	0.536272	0
H	7	0.541973	0.578402	0
H	8	-0.30508	0.410637	0
H	9	-0.34243	0.430895	0
H	10	-0.49653	0.333129	0
H	11	-0.44786	0.304041	0
H	12	-0.09847	0.507841	0
H	13	-0.53627	0.041904	0
H	14	-0.5784	-0.03643	0
H	15	-0.41064	-0.71572	0
H	16	-0.4309	-0.77333	0
H	17	-0.33313	-0.82966	0
H	18	-0.30404	-0.7519	0
H	19	-0.50784	-0.60631	0
H	20	-0.0419	-0.57818	0
H	21	0.036429	-0.54197	0
H	22	-0.71572	-0.30508	0
H	23	-0.77333	-0.34243	0
H	24	-0.82966	-0.49653	0
H	25	-0.7519	-0.44786	0
H	26	-0.60631	-0.09847	0
H	27	-0.57818	-0.53627	0
H	28	-0.54197	-0.5784	0
H	29	0.305078	-0.41064	0
H	30	0.342434	-0.4309	0
H	31	0.496532	-0.33313	0
H	32	0.447861	-0.30404	0
H	33	0.098466	-0.50784	0
H	34	0.536272	-0.0419	0

H	35	0.578402	0.036429	0
H	36	0.410637	0.715716	0
H	37	0.430895	0.773329	0
H	38	0.333129	0.829661	0
H	39	0.304041	0.751901	0
H	40	0.507841	0.606308	0
H	41	0.041904	0.578175	0
H	42	-0.03643	0.541973	0
C	1	0.693976	0.318216	0
C	2	0.710249	0.361416	0
C	3	0.634667	0.243323	0
C	4	0.785438	0.377138	0
C	5	0.842803	0.445471	0
C	6	0.816407	0.461638	0
C	7	0.773775	0.434882	0
C	8	0.585035	0.112149	0
C	9	0.520351	0.476794	0
C	10	0.54298	0.520006	0
C	11	0.523043	0.543207	0
C	12	-0.31822	0.375761	0
C	13	-0.36142	0.348834	0
C	14	-0.24332	0.391344	0
C	15	-0.37714	0.4083	0
C	16	-0.44547	0.397332	0
C	17	-0.46164	0.354769	0
C	18	-0.43488	0.338893	0
C	19	-0.11215	0.472886	0
C	20	-0.47679	0.043557	0
C	21	-0.52001	0.022974	0
C	22	-0.54321	-0.02016	0
C	23	-0.37576	-0.69398	0
C	24	-0.34883	-0.71025	0
C	25	-0.39134	-0.63467	0
C	26	-0.4083	-0.78544	0
C	27	-0.39733	-0.8428	0
C	28	-0.35477	-0.81641	0
C	29	-0.33889	-0.77378	0
C	30	-0.47289	-0.58504	0
C	31	-0.04356	-0.52035	0
C	32	-0.02297	-0.54298	0
C	33	0.020163	-0.52304	0

C	34	-0.69398	-0.31822	0
C	35	-0.71025	-0.36142	0
C	36	-0.63467	-0.24332	0
C	37	-0.78544	-0.37714	0
C	38	-0.8428	-0.44547	0
C	39	-0.81641	-0.46164	0
C	40	-0.77378	-0.43488	0
C	41	-0.58504	-0.11215	0
C	42	-0.52035	-0.47679	0
C	43	-0.54298	-0.52001	0
C	44	-0.52304	-0.54321	0
C	45	0.318216	-0.37576	0
C	46	0.361416	-0.34883	0
C	47	0.243323	-0.39134	0
C	48	0.377138	-0.4083	0
C	49	0.445471	-0.39733	0
C	50	0.461638	-0.35477	0
C	51	0.434882	-0.33889	0
C	52	0.112149	-0.47289	0
C	53	0.476794	-0.04356	0
C	54	0.520006	-0.02297	0
C	55	0.543207	0.020163	0
C	56	0.375761	0.693976	0
C	57	0.348834	0.710249	0
C	58	0.391344	0.634667	0
C	59	0.4083	0.785438	0
C	60	0.397332	0.842803	0
C	61	0.354769	0.816407	0
C	62	0.338893	0.773775	0
C	63	0.472886	0.585035	0
C	64	0.043557	0.520351	0
C	65	0.022974	0.54298	0
C	66	-0.02016	0.523043	0
N	1	0.82669	0.403997	0
N	2	0.542689	0.454835	0
N	3	-0.404	0.422694	0
N	4	-0.45484	0.087854	0
N	5	-0.42269	-0.82669	0
N	6	-0.08785	-0.54269	0
N	7	-0.82669	-0.404	0
N	8	-0.54269	-0.45484	0

N	9	0.403997	-0.42269	0
N	10	0.454835	-0.08785	0
N	11	0.422694	0.82669	0
N	12	0.087854	0.542689	0

Table S4. Fractional atomic coordinates for the unit cell of **Q-COF**

Element	Atom Number	<i>x</i>	<i>y</i>	<i>z</i>
H	1	0.568073	0.334546	0
H	2	0.694958	0.443576	0
H	3	0.664385	0.491846	0
H	4	0.588102	0.302987	0
H	5	0.4327	0.66713	0
H	6	0.306711	0.556837	0
H	7	0.338108	0.509572	0
H	8	0.412183	0.69814	0
H	9	0.362328	0.478229	0
H	10	0.72001	0.651164	0
H	11	0.689284	0.69918	0
H	12	0.610511	0.668431	0
H	13	0.331002	0.426669	0
H	14	0.283042	0.347845	0
H	15	0.313708	0.299924	0
H	16	0.392625	0.330704	0
H	17	0.479148	0.119882	0
H	18	0.427317	0.099589	0
H	19	0.96723	0.546421	0
H	20	0.968935	0.559473	0
H	21	0.549578	0.578334	0
H	22	0.562536	0.58962	0
H	23	-0.33455	0.233527	0
H	24	-0.44358	0.251383	0
H	25	-0.49185	0.172539	0
H	26	-0.30299	0.285116	0
H	27	-0.66713	-0.23443	0
H	28	-0.55684	-0.25013	0
H	29	-0.50957	-0.17147	0
H	30	-0.69814	-0.28596	0
H	31	-0.47823	-0.1159	0
H	32	-0.65116	0.068847	0
H	33	-0.69918	-0.0099	0
H	34	-0.66843	-0.05792	0
H	35	-0.42667	-0.09567	0

H	36	-0.34785	-0.0648	0
H	37	-0.29992	0.013784	0
H	38	-0.3307	0.061921	0
H	39	-0.11988	0.359266	0
H	40	-0.09959	0.327728	0
H	41	-0.54642	0.42081	0
H	42	-0.55947	0.409462	0
H	43	-0.57833	-0.02876	0
H	44	-0.58962	-0.02708	0
H	45	-0.23353	-0.56807	0
H	46	-0.25138	-0.69496	0
H	47	-0.17254	-0.66439	0
H	48	-0.28512	-0.5881	0
H	49	0.23443	-0.4327	0
H	50	0.250125	-0.30671	0
H	51	0.171465	-0.33811	0
H	52	0.285957	-0.41218	0
H	53	0.115901	-0.36233	0
H	54	-0.06885	-0.72001	0
H	55	0.009895	-0.68928	0
H	56	0.057921	-0.61051	0
H	57	0.095667	-0.331	0
H	58	0.064803	-0.28304	0
H	59	-0.01378	-0.31371	0
H	60	-0.06192	-0.39263	0
H	61	-0.35927	-0.47915	0
H	62	-0.32773	-0.42732	0
H	63	-0.42081	-0.96723	0
H	64	-0.40946	-0.96894	0
H	65	0.028756	-0.54958	0
H	66	0.027084	-0.56254	0
C	1	0.484547	0.526029	0
C	2	0.458132	0.482541	0
C	3	0.475085	0.456107	0
C	4	0.518512	0.473025	0
C	5	0.54496	0.516653	0
C	6	0.528062	0.543038	0
C	7	0.579065	0.463757	0
C	8	0.599379	0.439731	0
C	9	0.589679	0.369827	0
C	10	0.632969	0.386549	0

C	11	0.65969	0.429998	0
C	12	0.64281	0.45656	0
C	13	0.649945	0.359902	0
C	14	0.623377	0.316612	0
C	15	0.424081	0.535389	0
C	16	0.402955	0.562303	0
C	17	0.411536	0.631781	0
C	18	0.368077	0.614343	0
C	19	0.342054	0.570972	0
C	20	0.359349	0.544909	0
C	21	0.350684	0.640555	0
C	22	0.376847	0.684057	0
C	23	0.605435	0.507052	0
C	24	0.588375	0.533519	0
C	25	0.397623	0.492001	0
C	26	0.414684	0.465534	0
C	27	0.614833	0.576907	0
C	28	0.388177	0.422043	0
C	29	0.658342	0.594068	0
C	30	0.684712	0.637364	0
C	31	0.667755	0.663886	0
C	32	0.624292	0.646916	0
C	33	0.597837	0.603441	0
C	34	0.34475	0.405126	0
C	35	0.318347	0.361689	0
C	36	0.335248	0.335216	0
C	37	0.378855	0.352229	0
C	38	0.405222	0.395613	0
C	39	-0.52603	-0.04148	0
C	40	-0.48254	-0.02441	0
C	41	-0.45611	0.018977	0
C	42	-0.47303	0.045487	0
C	43	-0.51665	0.028307	0
C	44	-0.54304	-0.01498	0
C	45	-0.46376	0.115309	0
C	46	-0.43973	0.159649	0
C	47	-0.36983	0.219852	0
C	48	-0.38655	0.246421	0
C	49	-0.43	0.229693	0
C	50	-0.45656	0.18625	0
C	51	-0.3599	0.290043	0

C	52	-0.31661	0.306765	0
C	53	-0.53539	-0.11131	0
C	54	-0.5623	-0.15935	0
C	55	-0.63178	-0.22025	0
C	56	-0.61434	-0.24627	0
C	57	-0.57097	-0.22892	0
C	58	-0.54491	-0.18556	0
C	59	-0.64056	-0.28987	0
C	60	-0.68406	-0.30721	0
C	61	-0.50705	0.098383	0
C	62	-0.53352	0.054856	0
C	63	-0.492	-0.09438	0
C	64	-0.46553	-0.05085	0
C	65	-0.57691	0.037926	0
C	66	-0.42204	-0.03387	0
C	67	-0.59407	0.064273	0
C	68	-0.63736	0.047348	0
C	69	-0.66389	0.003869	0
C	70	-0.64692	-0.02263	0
C	71	-0.60344	-0.0056	0
C	72	-0.40513	-0.06038	0
C	73	-0.36169	-0.04334	0
C	74	-0.33522	0.000032	0
C	75	-0.35223	0.026626	0
C	76	-0.39561	0.009609	0
C	77	0.041482	-0.48455	0
C	78	0.024409	-0.45813	0
C	79	-0.01898	-0.47509	0
C	80	-0.04549	-0.51851	0
C	81	-0.02831	-0.54496	0
C	82	0.014976	-0.52806	0
C	83	-0.11531	-0.57907	0
C	84	-0.15965	-0.59938	0
C	85	-0.21985	-0.58968	0
C	86	-0.24642	-0.63297	0
C	87	-0.22969	-0.65969	0
C	88	-0.18625	-0.64281	0
C	89	-0.29004	-0.64995	0
C	90	-0.30677	-0.62338	0
C	91	0.111307	-0.42408	0
C	92	0.159348	-0.40296	0

C	93	0.220246	-0.41154	0
C	94	0.246265	-0.36808	0
C	95	0.228919	-0.34205	0
C	96	0.18556	-0.35935	0
C	97	0.289871	-0.35068	0
C	98	0.307209	-0.37685	0
C	99	-0.09838	-0.60544	0
C	100	-0.05486	-0.58838	0
C	101	0.094378	-0.39762	0
C	102	0.050851	-0.41468	0
C	103	-0.03793	-0.61483	0
C	104	0.033866	-0.38818	0
C	105	-0.06427	-0.65834	0
C	106	-0.04735	-0.68471	0
C	107	-0.00387	-0.66776	0
C	108	0.022625	-0.62429	0
C	109	0.005604	-0.59784	0
C	110	0.060376	-0.34475	0
C	111	0.043343	-0.31835	0
C	112	-3.2E-05	-0.33525	0
C	113	-0.02663	-0.37886	0
C	114	-0.00961	-0.40522	0
N	1	0.467502	0.552459	0
N	2	0.535501	0.446643	0
N	3	0.572866	0.396392	0
N	4	0.428975	0.605762	0
N	5	-0.55246	-0.08496	0
N	6	-0.44664	0.088858	0
N	7	-0.39639	0.176474	0
N	8	-0.60576	-0.17679	0
N	9	0.084957	-0.4675	0
N	10	-0.08886	-0.5355	0
N	11	-0.17647	-0.57287	0
N	12	0.176787	-0.42898	0

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