A Quinoxaline-based Porous Organic Polymer Containing Copper Nanoparticles CuNPs@Q-POP as a Robust Nanocatalyst toward C-N Coupling Reaction

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Experimental Section

Materials and instruments:

All chemicals were purchased from commercial sources and used without further purification. Solvents used in this study were dried and purified using standard procedures before usage. The powder X-ray diffraction (XRD) patterns of samples were performed on a D8 Advance Bruker X-ray diffractometer using Cu Kα (λ=1.54 Å) radiation. Nitrogen sorption isotherms were carried out using a BEL sorb-mini 2 at 77 K. The specific surface areas and the pore size distributions of materials were determined by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model, respectively. Before analysis, the samples were outgassed at 120 °C for 4h under vacuum. The Fourier transform infrared (FT-IR) spectra were recorded on Jasco FTIR-6300spectrometer as KBr pellets. Thermal gravimetric analysis (TGA) was obtained using an SDT Q600 instrument by heating samples from 25 to 600 °C in a dynamic argon atmosphere with a heating rate of 10°C min⁻¹. Field-emission scanning electron (FE-SEM) microscopy and energy-dispersive X-ray spectroscopy (EDX) analysis were carried out on a Tescan Mira3 scanning electron microscope. Transmission electron microscopy (TEM) images were performed on Philips-CM120. Inductively coupled plasma (ICP) was measured on an Analytic Jena PQ9000 for the determination of Cu content. Conversion and selectivity were determined by GC-FID on a Shimadzu GC-16A instrument using EtOAc-Hexane (1:5) as eluent. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer.

Synthesis of bis(salicylidene)-O-phenylene diamine (A):

This compound was prepared according to the procedure reported in the literature. O-phenylenediamine (2.16 g, 20 mmol) and salicylaldehyde (4.24 mL, 40 mmol) were dissolved in dry methanol (40 mL) at room temperature. After stirring for 16 h, the resulting solid was separated by filtration. The obtained solid was washed with methanol and dried in vacuo to afford compound (A) as yellow powders (6 g, 95%).

Synthesis of 2,3-di(2-hydroxyphenyl)1,2-dihydro quinoxaline (B):

Under an argon atmosphere, NaCN (0.226 g, 4.6 mmol) was introduced into a solution of bis(salicylidene)-O-phenylenediamine (3.7 g, 11.8 mmol) in dry DMF (35 mL), and the mixture was stirred at room temperature for 48 h. Subsequently, the reaction mixture was poured into ice water (50 mL). The resultant solid was filtered via Buchner funnel, washed with water for several times and dried. The crude product was purified by recrystallization in acetonitrile. Finally, the pure desired product was obtained as an orange solid (2.96 g, 80%). ¹H-NMR (400 MHz, CDCl₃): δ 14.92 (s, 1H), 10.18 (s, 1H), 7.44 (d, J=8 Hz, 1H), 7.33-7.29 (m, 1H), 7.24 (d, J=8 Hz, 1H), 7.08-7.04 (m, 1H), 7.01-6.96 (m, 1H), 6.92-6.86 (m, 4H), 6.81-
Synthesis of allyl-functionalized 2,3-di(2-hydroxy phenyl)1,2-dihydroquinoxaline (C):
A solution of 2,3-di(2-hydroxyphenyl)1,2-dihydro quinoxaline (2.96 g, 9.4 mmol) in acetone (60 mL) was shaken with K$_2$CO$_3$ (3.9 g, 28.2 mmol). Allyl bromide (2.44 mL, 28.2 mmol) was then added slowly to the solution. After the mixture was stirred at room temperature for 48 h, water was added (20 mL) and the product was extracted with ethyl acetate (3×30 mL) and dried over MgSO$_4$. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel (EtOAc/hexane 1:4) to yield allyl functionalized 2,3-di(2-hydroxyphenyl)1,2-dihydroquinoxaline monomer as an orange powder (1.86 g, 50%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 14.98 (s, 1H), 7.31 (d, $J=8$ Hz, 1H), 7.31 (d, $J=8$ Hz, 1H), 6.88 (d, $J=8$ Hz, 1H), 6.79 (d, $J=8$ Hz, 1H), 6.71-6.64 (m, 3H), 6.55 (d, $J=8$ Hz, 1H), 6.30 (s, 1H), 6.14-6.07 (m, 1H), 5.61-5.54 (m, 1H), 5.46 (dd, $J=18$ Hz, $J=4$ Hz, 1H), 5.32 (dd, $J=10$ Hz, $J=4$ Hz, 1H), 5.03 (dd, $J=18$ Hz, $J=4$ Hz, 1H), 4.97 (dd, $J=12$ Hz, $J=4$ Hz, 1H), 4.63-4.62 (m, 2H), 3.92-3.91 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 161.5, 160.0, 152.3, 135.8, 132.6, 131.9, 131.3, 129.9, 128.9, 128.1, 127.9, 126.4, 126.3, 125.5, 120.8, 117.2, 116.9, 116.6, 116.5, 115.5, 111.3, 110.5, 68.0, 50.6, 50.5.

Synthesis of Q-POP:
Radical copolymerization of ligand C with divinylbenzene (DVB) as cross-linker, in the presence of azobisisobutyronitrile (AIBN) as a radical initiator, was used to synthesis the nanoporous polymer under solvothermal conditions. Typically, the monomer C (1 g, 2.52 mmol) and divinylbenzene (1.43 mL, 10.1 mmol) were dissolved in dry DMF (10 mL), followed by the addition of AIBN (0.05 g). The reaction mixture was degassed with argon gas for 30 min, poured into a 50 mL autoclave (stainless steel 316), and heated at 100 °C for 24 h. After cooling to room temperature, water (30 mL) was added to the reaction mixture and the resulting polymer was filtered and washed with excess water. Additionally, the as-prepared polymer was further washed with methanol for the elimination of any unreacted monomer C. Finally, the desired polymer was obtained as a yellow powder and dried in an oven at 90-100 °C overnight.

Synthesis of CuNPs@Q-POP(7.3% Cu):
To a round-bottom flask were introduced Q-POP (1.5 g), MeOH (50 mL), and Et$_3$N (1 mL). The resultant suspension was allowed to stir at room temperature for 1 h. Then, Cu(NO$_3$)$_2$.3H$_2$O (0.8 g) in MeOH (20 mL) was added to the above suspension and refluxed for about 12 h. The green Cu$^{2+}$@Q-POP was isolated by filtration, washed with MeOH for removal of excess Cu(NO$_3$)$_2$.3H$_2$O, and then dried in vacuo for
overnight. Next, CuNPs@Q-POP were synthesized by the reduction of Cu$^{2+}$@Q-POP. An aqueous solution of hydrazine hydrate (10 mL, 35%) was added dropwise with vigorous stirring under argon atmosphere to a mixture of Cu$^{2+}$@Q-POP (1.5 g), EtOH (17.5 mL), H$_2$O (10 mL), and NH$_4$OH (17.5 mL, 25%). Afterward, the mixture was transferred into a 100 mL stainless steel autoclave and treated at 100 °C for 4 h. Finally, the mixture was filtered and washed with water and methanol successively. The resultant brown solid was dried under a vacuum to obtain CuNPs@Q-POP. Inductively coupled plasma (ICP) analysis displayed a Cu content of 7.3% in the CuNPs@Q-POP.

**Synthesis of CuNPs@Q-POP(2.8% Cu):**

To a round-bottom flask, Q-POP (1.5 g) was suspended in a mixture of MeOH (50 mL) and Et$_3$N (1 mL). The resultant suspension was allowed to stir at room temperature for 1 h. Then, Cu(NO$_3$)$_2$.3H$_2$O (0.2 g) in MeOH (6 mL) was added and refluxed for about 12 h and the resultant green Cu$^{2+}$@Q-POP precipitate was filtered, washed with MeOH, and dried in vacuo overnight. Next, an aqueous solution of hydrazine hydrate (5 mL, 35%) was added dropwise with intense stirring under argon atmosphere to the mixture of Cu$^{2+}$@Q-POP (1.5 g), EtOH (17.5 mL), H$_2$O (10 mL), and NH$_4$OH (17.5 mL, 25%). Then, the mixture was heated at 100 °C for 4 h in an appropriate stainless steel autoclave. Finally, the mixture was filtered and successively washed with water and methanol. Thereafter, the brown solid was dried under vacuum to obtain CuNPs@Q-POP. Inductively coupled plasma (ICP) analysis revealed that the Cu content of CuNPs@Q-POP was 2.8%.

**General procedure for N-arylation of anilines with aryl halides catalyzed by CuNPs@Q-POP(2.8% Cu):**

In a 25 mL round bottom flask (two necked-flask) a mixture of aryl halide (1 mmol), aniline (1.2 mmol), K$_2$CO$_3$ (2 mmol), PEG-200 (2 mL), and CuNPs@Q-POP(2.8% Cu) catalyst (75 mg) was stirred under nitrogen atmosphere at 110 °C for 24. After the reaction, ethyl acetate (10 mL) was added to the reaction mixture and the catalyst was separated by filtration and washed with ethyl acetate. Then, water (10 mL) was added to the filtrate and further extracted with ethyl acetate (2 × 10 mL). The extracted organic phases were combined and dried with anhydrous MgSO$_4$. The organic phase was analyzed by GC to determine conversion and selectivity. The conversions were assessed according to the concentration of iodobenzene. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel to obtain the desired product. The product was analyzed by $^1$H-NMR and $^{13}$C-NMR.

**General procedure for recyclability of the catalyst.**
To examine the recyclability of CuNPs@Q-POP, the $N$-arylation of iodobenzene with aniline was performed under the similar condition as mentioned above. After the completion of the reaction, the catalyst was separated from the mixture reaction by filtration and washed three times with water, ethyl acetate, and methanol, then dried under vacuum at 100°C for 12h. Finally, the reused catalyst was exerted for the next run under optimum condition.

**CCDC Number: 1953774**

![ORTEP representation of compound B.](image)

**Table 1. Crystal data and structure refinement for compound B.**

|                         |               |
|-------------------------|---------------|
| Identification code     | shelx         |
| Empirical formula       | C20 H16 N2 O2 |
| Formula weight          | 316.35        |
| Temperature             | 298(2) K      |
| Wavelength              | 0.71073 Å     |
Crystal system, space group       Monoclinic,  P 21/c

Unit cell dimensions              a = 9.7420(19) A   alpha = 90 deg.
       b = 16.082(3) A   beta = 115.05(3) deg.
       c = 11.405(2) A   gamma = 90 deg.

Volume                            1618.6(7) A^3

Z, Calculated density             4,  1.298 Mg/m^3

Absorption coefficient           0.085 mm^-1

F(000)                            664

Theta range for data collection   2.533 to 24.998 deg.

Limiting indices                  -11<=h<=11, -18<=k<=19, -13<=l<=13

Reflections collected / unique   10238 / 2860 [R(int) = 0.1897]

Completeness to theta = 24.998   99.9 %

Refinement method                 Full-matrix least-squares on F^2

Data / restraints / parameters    2860 / 1 / 226

Goodness-of-fit on F^2           0.827

Final R indices [I>2sigma(I)]    R1 = 0.0721, wR2 = 0.1622

R indices (all data)             R1 = 0.1269, wR2 = 0.1852

Largest diff. peak and hole       0.227 and -0.311 e.A^-3

Table 1.  Bond lengths [A] and angles [deg] for compound B.

| Bond             | Length [A]  |
|------------------|-------------|
| O(1)-C(2)        | 1.358(4)    |
| O(1)-H(1)        | 0.8200      |
| O(2)-C(14)       | 1.345(4)    |
| O(2)-H(2)        | 0.821(2)    |
| N(1)-C(8)        | 1.295(4)    |
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| N(1)-C(15)            | 1.397(4)     |
| C(8)-C(9)             | 1.460(4)     |
| C(8)-C(7)             | 1.525(4)     |
| C(7)-N(2)             | 1.467(4)     |
| C(7)-C(1)             | 1.524(4)     |
| C(1)-C(6)             | 1.387(4)     |
| C(1)-C(2)             | 1.416(4)     |
| C(9)-C(10)            | 1.408(5)     |
| C(9)-C(14)            | 1.425(4)     |
| N(2)-C(20)            | 1.388(4)     |
| N(2)-H(2A)            | 0.99(4)      |
| C(3)-C(4)             | 1.368(5)     |
| C(3)-C(2)             | 1.383(5)     |
| C(6)-C(5)             | 1.372(5)     |
| C(15)-C(16)           | 1.391(5)     |
| C(15)-C(20)           | 1.406(5)     |
| C(13)-C(12)           | 1.368(6)     |
| C(13)-C(14)           | 1.376(5)     |
| C(10)-C(11)           | 1.372(5)     |
| C(20)-C(19)           | 1.375(5)     |
| C(4)-C(5)             | 1.402(5)     |
| C(16)-C(17)           | 1.364(6)     |
| C(12)-C(11)           | 1.402(6)     |
| C(19)-C(18)           | 1.377(6)     |
| Bond                  | Angle (Degrees) |
|----------------------|-----------------|
| C(18)-C(17)         | 1.384(6)        |
| C(8)-N(1)-C(15)     | 120.1(3)        |
| N(1)-C(8)-C(9)      | 118.3(3)        |
| N(1)-C(8)-C(7)      | 120.1(3)        |
| C(9)-C(8)-C(7)      | 121.6(3)        |
| N(2)-C(7)-C(1)      | 113.8(3)        |
| N(2)-C(7)-C(8)      | 106.0(2)        |
| C(1)-C(7)-C(8)      | 111.5(2)        |
| C(6)-C(1)-C(2)      | 120.6(3)        |
| C(6)-C(1)-C(7)      | 124.5(3)        |
| C(10)-C(9)-C(14)    | 117.8(3)        |
| C(10)-C(9)-C(8)     | 121.6(3)        |
| C(14)-C(9)-C(8)     | 121.6(3)        |
| C(20)-N(2)-C(7)     | 115.9(3)        |
| C(4)-C(3)-C(2)      | 120.6(3)        |
| O(1)-C(2)-C(3)      | 123.9(3)        |
| O(1)-C(2)-C(1)      | 116.5(3)        |
| C(3)-C(2)-C(1)      | 119.6(3)        |
| C(5)-C(6)-C(1)      | 122.0(3)        |
| C(16)-C(15)-N(1)    | 120.4(3)        |
| C(16)-C(15)-C(20)   | 119.5(3)        |
| N(1)-C(15)-C(20)    | 119.8(3)        |
| C(12)-C(13)-C(14)   | 121.5(4)        |
Figure S1. Wide angle powder XRD patterns of reused CuNPs@Q-POP for N-arylation of iodobenzene with aniline.
Figure S2. SEM image of reused CuNPs@Q-POP for N-arylation of iodobenzene with aniline.

The NMR spectral data of the products

N-phenylaniline

![N-phenylaniline](image)

White solid, m.p. 52-53 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm)=7.33-7.28 (m, 4H), 7.12-7.10 (m, 4H), 6.99-6.95 (m, 2H), 5.73 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm)=142.6, 128.9, 120.5, 117.3.

N-(4-methoxyphenyl)aniline

![N-(4-methoxyphenyl)aniline](image)

Pale yellow solid, m.p. 103 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm)= 7.17-7.12 (m, 2H), 7.03-6.99 (m, 2H), 6.86-6.74 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm)=155.3, 145.2, 135.7, 129.3, 122.2, 119.6, 115.6, 114.7, 55.6.

N-(4-methylphenyl)aniline
Pale yellow solid, m.p. 81 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm)=7.17-7.15 (m, 2H), 7.03-7.01 (m, 2H), 6.95-6.92 (m, 4H), 6.83-6.79 (m, 1H), 5.53 (s, 1H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm)=130.9, 129.8, 129.7, 129.3, 122.7, 120.3, 118.9, 116.9, 20.7.

$N$-(2-methoxyphenyl)aniline

$N$-(3-methoxyphenyl)aniline

$N$-(4-nitrophenyl)aniline

Yellow solid, m.p. 130 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm)=8.05 (d, $J$=8 Hz, 2H), 7.34-7.30 (m, 2H), 7.15-7.08 (m, 3H), 6.87 (d, $J$=8 Hz, 2H), 6.21 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm)=150.3, 139.7, 139.5, 129.7, 126.2, 124.7, 121.9, 113.7.

$N$-(4-chlorophenyl)aniline
Pale yellow solid, m.p. 71-72 °C; $^1$H NMR (400 MHz, CDCl3): $\delta$ (ppm)=7.23-7.20 (m, 2H), 7.14 (d, $J$=8 Hz, 2H), 6.99-6.97 (m, 2H), 6.92 (d, $J$=8 Hz, 2H), 6.88-6.87 (m, 1H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ (ppm)=142.6, 141.9, 129.4, 129.3, 121.5, 118.8, 118.1.

$N$-(2-chlorophenyl)aniline

Yellowish oil; $^1$H NMR (400 MHz, CDCl3): $\delta$ (ppm)=7.29-7.21 (m, 4H), 7.10-7.03 (m, 3H), 6.97 (t, $J$=8 Hz, 1H), 6.75-6.71 (m, 1H), 6.03 (s, 1H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ (ppm)=141.5, 129.7, 129.4, 127.4, 122.6, 120.4, 120.2, 115.5.

$N$-phenylindole

Colorless solid, m.p. 60-62 °C; $^1$H NMR (400 MHz, CDCl3): $\delta$ (ppm)=7.79-7.76 (m, 1H), 7.66-7.64 (m, 1H), 7.59-7.56 (m, 4H), 7.44-7.40 (m, 2H), 7.33-7.25 (m, 2H), 6.77-6.76 (m, 1H); $^{13}$C NMR (100 MHz, CDCl3): $\delta$ (ppm)=139.9, 135.9, 129.7, 129.4, 128.0, 126.5, 124.4, 122.4, 121.2, 120.4, 110.6, 103.6.
Copies of $^1$H NMR and $^{13}$C NMR spectra
H

OMe

N

[Chemical structure diagram]

[1H NMR spectrum]

[13C NMR spectrum]
