[Supporting Information]

Eosin Y Dye-based Porous Organic Polymer for Highly Efficient Heterogeneous Photocatalytic Dehydrogenative Coupling Reaction

Chang-An Wang*, Yan-Wei Li, Xue-Li Cheng, Jian-Ping Zhang, and

Yin-Feng Han*

College of Chemistry and Chemical Engineering, Taishan University, Tai'an, Shandong 271021, P. R. China. E-mail: wangcha chem@163.com

- A. The permanent porosity of EY-POPs
- B. BET surface area plot for **EY-POP-1** and **EY-POP-2** calculated from the isotherm
- C. N₂ adsorption-desorption isotherms of recycled catalyst
- D. General procedure for the dehydrogenative coupling reaction
- E. Recyclability of EY-POP-1 catalyst
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A. The permanent porosity of EY-POPs

Table S1. The permanent porosity of EY-POP-1 and EY-POP-2

Polymer	Building Blocks		Molar	\mathbf{S}_{BET}	S _{micro}	V_{total}	V _{micro}
	Functional	Structural	Ratio	$(m^2g^{-1})^a$	$(m^2g^{-1})^b$	$(cm^3g^{-1})^c$	$(cm^3g^{-1})^b$
EY-POP-1	1	2	3:4	587	384	0.33	0.16
EY-POP-2	1	3	1:1	718	535	0.37	0.22

^{*a*} surface area calculated from the N₂ adsorption isotherm using the BET method. ^{*b*} Micro surface area and micropore volume calculated using the t-plot method. ^{*c*} Total pore volume at $P/P_0 = 0.99$

B. BET surface area plot for **EY-POP-1** and **EY-POP-2** calculated from the isotherm



Figure S1. BET surface area plot for EY-POP-1 calculated from the isotherm



Figure S2. BET surface area plot for EY-POP-2 calculated from the isotherm



C. N₂ adsorption-desorption isotherms of recycled catalyst

Figure S3. N_2 adsorption-desorption isotherms of the recycled EY-POP-1 catalyst after six-time catalytic reaction. The result imply that the decrease of catalytic activity of the recycled catalyst may come from the partial blocking of polymeric nanopores.

D. General procedure for the dehydrogenative coupling reaction

run of catalytic activity test of In a typical EY-POP-1, N-Aryltetradroisoquinolines (0.2 mmol), nitroalkane (1.0 mL), and EY-POP-1 (10 mg) were added into a 15-mL glass tube. The tube was sealed with a rubber stopper and the reaction mixture was connected to the air through a needle in the stopper. The tube was subsequently stirred at room temperature under irradiation with visible light using a cool daylight energy-saving bulb (14 W) until all starting material had been consumed. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with EtOAc (3 x 5 mL). The combined organic phase was then concentrated and purified by flash column chromatography with petroleum ether/EtOAc = 10:1 as the eluent to give the pure product.



1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (52.6 mg, 98%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.16 (m, 5 H), 7.11 (d, *J* = 7.0 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 6.83 (t, *J* = 7.3 Hz, 1 H), 5.53 (t, *J* = 7.2 Hz, 1 H), 4.85 (dd, *J* = 11.8, 7.8 Hz, 1 H), 4.54 (dd, *J* = 11.8, 6.6 Hz, 1 H), 3.65–3.59 (m, 2 H), 3.09–3.03 (m, 1 H), 2.77 (dt, *J* = 16.3, 4.9 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 148.37, 135.22, 132.86, 129.45, 129.14, 128.06, 126.94, 126.64, 119.36, 115.04, 78.71, 58.14, 42.00, 26.39.



1-(Nitromethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-methylphenyl) -1,2,3,4-

tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1- (nitromethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (53.2 mg, 94%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.24–7.12 (m, 4 H), 7.07 (t, *J* = 7.3 Hz, 2 H), 6.90–6.85 (m, 2 H), 5.51–5.47 (m, 1 H), 4.84 (dd, *J* = 11.8, 8.1 Hz, 1 H), 4.54 (dd, *J* = 11.8, 6.4 Hz, 1 H), 3.69–3.51 (m, 2 H), 3.13–2.97 (m, 1 H), 2.74 (dt, *J* = 16.4, 4.5 Hz, 1 H), 2.25 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 146.35, 135.32, 132.91, 129.94, 129.24, 129.08, 127.97, 126.94, 126.59, 115.87, 78.80, 58.36, 42.29, 26.20, 20.33.



1-(Nitromethyl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-fluorophenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1- (nitromethyl)-2-(4- fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (52.2 mg, 91%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.14 (m, 4 H), 6.97–6.88 (m, 4 H), 5.43 (dd, *J* = 8.5, 6.0 Hz, 1 H), 4.84 (dd, *J* = 12.0, 8.7 Hz, 1 H), 4.57 (dd, *J* = 12.0, 5.9 Hz, 1 H), 3.61–3.58 (m, 2 H), 3.16–2.97 (m, 1H), 2.72 (dt, *J* = 16.5, 4.1 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 158.34, 155.96, 145.27, 135.22, 132.52, 129.43, 128.07, 126.92, 126.74, 117.95, 117.88, 115.95, 115.73, 78.84, 58.70, 42.82, 25.76.



1-(Nitromethyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-chlorophenyl) -1,2,3,4-tetrahydroisoquinoline (48.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1- (nitromethyl)-2-(4- chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (59.1 mg, 98%) as a yellow soild. ¹H NMR (400 MHz, CDCl₃) δ 7.16–7.05 (m, 6 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 5.43–5.39 (m, 1 H), 4.76 (dt, *J* = 24.8, 12.4 Hz, 1 H), 4.49 (dd, *J* = 12.0, 6.3 Hz, 1 H), 3.56–3.52 (m, 2 H), 3.00 (ddd, *J* = 23.3, 16.9, 6.6 Hz, 1 H), 2.71 (dt, *J* = 16.4, 4.7

Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 146.93, 134.98, 132.36, 129.30, 129.27, 128.24, 126.91, 126.81, 124.55, 116.56, 78.59, 58.25, 42.35, 26.09.



1-(Nitromethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-bromophenyl) -1,2,3,4-tetrahydroisoquinoline (57.6 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1- (nitromethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (69.0 mg, 99%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.05 (m, 6 H), 6.77 (dd, *J* = 14.2, 9.0 Hz, 2 H), 5.41 (t, *J* = 7.2 Hz, 1 H), 4.77 (dt, *J* = 26.0, 13.0 Hz, 1 H), 4.50 (dd, *J* = 12.0, 6.4 Hz, 1 H), 3.56–3.52 (m, 2 H), 3.03–2.95 (m, 1 H), 2.73 (dt, *J* = 16.4, 4.8 Hz, 1 H). ¹³C NMR (10 MHz, CDCl₃) δ 147.28, 134.93, 132.30, 132.23, 129.26, 128.28, 126.92, 126.84, 116.88, 116.43, 111.82, 78.54, 58.18, 42.32, 26.12.



1-(Nitromethyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-methoxyphenyl) -1,2,3,4-tetrahydroisoquinoline (47.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1- (nitromethyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (59.0 mg, 99%) as a yellow soild. ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.14 (m, 4 H), 6.95 (dt, *J* = 8.9, 6.7 Hz, 2 H), 6.83 (d, *J* = 9.1 Hz, 2 H), 5.43–5.39 (m, 1 H), 4.90–4.87 (m, 1 H), 4.62–4.57 (m, 1 H), 3.76 (s, 3 H), 3.59 (dt, *J* = 11.2, 6.5 Hz, 2 H), 3.03 (dt, *J* = 15.9, 7.8 Hz, 1 H), 2.76 (dd, *J* = 24.3, 12.9 Hz, 1 H).



1-(Nitromethyl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(2-methoxyphenyl) -1,2,3,4-

tetrahydroisoquinoline (47.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (58.1 mg, 97%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.21–7.04 (m, 4 H), 6.94 (tt, *J* = 16.0, 8.0 Hz, 1 H), 6.86–6.70 (m, 3 H), 5.41 (dt, *J* = 32.0, 16.0 Hz, 1 H), 4.74 (dt, *J* = 16.1, 8.1 Hz, 1 H), 4.46 (dd, *J* = 12.1, 5.0 Hz, 1 H), 3.75 (s, 3 H), 3.59–3.48 (m, 1 H), 3.47– 3.34 (m, 1 H), 2.91 (ddd, *J* = 17.1, 11.3, 6.2 Hz, 1 H), 2.64 (d, *J* = 16.5 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 153.02, 138.75, 135.29, 133.55, 129.49, 127.53, 126.77, 126.39, 124.10, 121.89, 120.97, 112.41, 79.10, 58.13, 55.74, 42.93, 26.78.



1-(Nitromethyl)-2-(3-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the procedure, general EY-POP-1 (10)mg), 2-(3-methylphenyl) -1,2,3,4tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(3-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (53.2 mg, 94%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.14 (m, 5 H), 6.83–6.80 (m, 2 H), 6.71 (d, J = 7.4 Hz, 1 H), 5.56 (t, J = 7.2 Hz, 1 H), 4.89 (dt, J = 23.7, 11.8 Hz, 1 H), 4.58 (dd, J = 11.8, 6.7 Hz, 1 H), 3.67–3.54 (m, 1 H), 3.19–3.06 (m, 1 H), 2.82 (dt, J = 16.3, 5.0 Hz, 1 H), 2.34 (s, 3 H). ¹³C NMR (101 MHz, CDCl₃) δ 148.19, 139.31, 135.18, 132.83, 129.34, 129.15, 128.09, 126.92, 126.68, 120.63, 116.05, 112.33, 78.70, 58.29, 42.43, 26.45, 21.85.



1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (53.2 mg, 94%) as a orange oil. ¹H NMR (400 MHz, CDCl₃) Major diastereoisomer δ 7.31–7.10 (m, 6 H), 7.03 (t, *J* = 8.0 Hz, 2 H), 6.85 (t, *J* = 7.3 Hz, 1 H), 5.27 (d, *J* = 8.0 Hz, 1 H), 5.08 (dq, *J* = 13.5, 6.7 Hz, 1 H), 3.86 (ddd, *J* =

13.4, 8.0, 5.7 Hz, 1 H), 3.64–3.51 (m, 2 H), 3.07 (dt, J = 14.1, 7.0 Hz, 1 H), 2.98–2.92 (m, 1 H), 1.56 (d, J = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 7.31–7.10 (m, 6 H), 7.03 (t, J = 8.0 Hz, 2 H), 6.85 (t, J = 7.3 Hz, 1 H), 4.93 (dq, J = 13.7, 6.9 Hz, 1 H), 1.72 (d, J = 6.8 Hz, 3 H).



1-(1-Nitroethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the EY-POP-1 (10 general procedure, mg), 2-(4-bromophenyl) -1,2,3,4tetrahydroisoquinoline (57.6 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1nitroethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (65.1 mg, 90%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) Major diastereoisomer δ 7.32–7.03 (m, 6 H), 6.77 (dd, J = 9.2, 3.0 Hz, 2 H), 5.07 (d, J = 8.7 Hz, 1 H), 4.95–4.85 (m, 1 H), 3.49– 3.42 (m, 2 H), 3.02–2.90 (m, 1 H), 2.83 (ddd, J = 21.6, 13.8, 6.1 Hz, 1 H), 1.47 (d, J = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 5.12 (d, J = 8.8 Hz, 1 H). 4.79 (dq, J = 13.7, 6.8 Hz, 1 H), 3.89 (t, J = 6.5 Hz, 1 H), 3.78–3.67 (m, 1 H), 1.59 (d, J = 6.8 Hz, 3 H).



1-(1-Nitroethyl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **EY-POP-1** (10 mg), 2-(4-fluorophenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1-nitroethyl)-2-(4- fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (54.6 mg, 91%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) Major diastereoisomer δ 7.19–7.03 (m, 6 H), 6.96–6.84 (m, 2 H), 5.05–4.95 (m, 2 H), 3.59–3.33 (m, 2 H), 2.93 (ddd, *J* = 14.8, 8.7, 6.1 Hz, 1 H), 2.87 – 2.70 (m, 1 H), 1.48 (d, *J* = 6.3 Hz, 3 H). Minor diastereomer (representative signals): δ 4.89–4.75 (m, 2 H), 3.74 (ddd, *J* = 13.9, 8.7, 5.6 Hz, 2 H), 1.61 (d, *J* = 6.8 Hz, 3 H).



1-(1-Nitroethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the procedure, EY-POP-1 2-(4-methylphenyl) general (10 mg), -1,2,3,4tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1nitroethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (54.5 mg, 92%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃) Major diastereoisomer δ 7.27–7.13 (m, 4 H), 7.11–6.99 (m, 2 H), 6.92 (dd, J = 19.6, 9.3 Hz, 2 H), 5.19 (t, J = 9.1 Hz, 1 H), 5.06 (dq, J = 13.4, 6.7 Hz, 1 H), 3.69–3.45 (m, 2 H), 3.12–2.98 (m, 1 H), 2.98–2.81 (m, 1 H), 2.25 (s, 3 H), 1.55 (d, J = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 4.97–4.80 (m, 1 H), 3.83 (ddd, J = 13.5, 8.2, 5.6 Hz, 2 H), 2.27 (s, 3 H), 1.71 (dd, J = 6.6, 2.4 Hz, 3 H).

E. Recyclability of EY-POP-1 catalyst

The recycling experiment was performed by recovering the **EY-POP-1** catalyst using the centrifugation method. The recovered **EY-POP-1** catalyst was washed with EtOAc to remove the residual product and simply dried before resuse. We chose the Aza-Hery reaction of 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline to nitromethane to investigate the recyclability of **EY-POP-1** catalyst, and the results are summarized in Table S2.

	CI +	CH ₃ NO ₂ —	EY-POP-1 (10 mg) 14 W bulb light r.t. air	• 🗘	
Cycle	Time (h)	Yield (%) ^[b]	Cycle	Time (h)	Yield (%) ^[b]
1	12	98	7	17	94
2	12	96	8	24	94
3	12	96	9	30	95
4	12	96	10	36	95
5	14	97	11	48	95
6	17	95	12	48	94

Table S2. Recycling of EY-POP-1 catalyst for the Aza-Hery reaction. [a]

[a] General condition: 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (48.8 mg, 0.2 mmol), nitromethane (1.0 mL), and **EY-POP-1** (10 mg), r.t., 14 W household bulb, in air. [b] Isolated yield after silica gel column chromatography.

F. ¹H NMR and ¹³C NMR spectra of the products



















