Supporting Information

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SI Methods

Materials Synthesis: Hybrid Polarizing Solids 1.0, 2.0, and 1.2.

1) Synthesis of hybrid polarizing solid 1.0. MatPrN$_3$ 1/X, MatPrNH$_2$ 1/X, and MatTEMPO 1/X [renamed hybrid polarizing solid 1.0 (HYPSO 1.0)] were prepared according to the literature (1).

2) Synthesis of HYPSO 2.0.

O-propargyl 2,2,6,6-tetramethyl-piperidine-1-oxyl. Under an argon atmosphere, NaH (2.72 g, 67.9 mmol) was added to dry *N,N*-dimethylformamide (DMF) (300 mL) and cooled to 0 °C (2). To this suspension, 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO; 9.00 g, 52.2 mmol) was added in portions. The reaction mixture was stirred for 30 min at 25 °C and then, cooled again to 0 °C before propargyl bromide (80% wt in toluene, 10.1 g, 67.9 mmol) was added dropwise. The resulting reaction mixture was then stirred for 3 h at 25 °C. Then, H$_2$O (300 mL) was added, and the product was extracted with EtOAc (3 × 150 mL). The combined organic layers were dried with brine and Na$_2$SO$_4$ and fully concentrated in vacuo. Column chromatography [heptane → 10% (vol/vol) EtOAc in heptane] yielded O-propargyl TEMPO (6.93 g, 63%) as an orange solid.

HYPSO 2.0. Under an argon atmosphere, O-propargyl TEMPO (369 mg, 1.75 mmol) was added to a suspension of MatPrN$_3$ 1/140 (3.00 g, 0.351 mmol azide) in DMF (40 mL) and Et$_3$N (1.5 mL). Then, a solution of CuI (3.3 mg, 18 μmol) in DMF/Et$_3$N (1:1; 500 μL) was added. The mixture was stirred for 48 h at 50 °C, filtrated, and washed with DMF (2 × 20 mL), EtOH (3 × 20 mL), and Et$_2$O (2 × 20 mL). The product was dried under vacuum (10^{-5} mbar) at 100 °C for 15 h.

3) Preparation of HYPSO 1.2.

Trityl alcohol. Tritert-butyl 8,8',8''-(hydroxymethanetriyl)Tris(2,2,6,6-tetramethylbenzo[1,2-d:4,5-d']bis([1,3]dithiole)-4-carboxylate) was prepared according to the literature (3).

HYPSO 1.2. Trityl alcohol (226 mg, 0.190 mmol) was dissolved in trifluoroacetic acid (TFA) (12 mL) and stirred under an argon atmosphere for 24 h. Then, the TFA was carefully evaporated in vacuo and replaced by dry dichloromethane (DCM) (5 mL). Oxalyl chloride (316 mg, 2.49 mmol) was dropwise added, and finally, two drops of dry DMF were added. The mixture was stirred for 4 h, during which time the color changed from yellow/dark brown to dark red. The solvent was evaporated until dryness, and the resulting red solid was redissolved in dry DCM (5 mL). To this solution, *N,N*-diisopropylethylamine (DIPEA) (33 μL, 0.19 mmol), 4-dimethylaminopyridine (DMAP) (2 mg, 20 μmol), and MatPrNH$_2$ 1/55 (500 mg, 0.146 mmol) were added. The mixture was stirred vigorously for 48 h, after which H$_2$O (1 mL) and DIPEA (60 μL, 0.38 mmol) were added. The mixture was stirred for 1 h to hydrolyze the unreacted acyl chlorides moieties (color changed from red to green), and then, it was filtrated, washed with DCM (3 × 5 mL) and Et$_2$O (3 × 5 mL), and dried under high vacuum (10^{-5} mbar) at 135 °C for 15 h (Tables S1 and S2).

Sample Preparation for Dissolution Dynamic Nuclear Polarization. Three different solutions were prepared.

i) Sodium [1-^{13}C]-pyruvate (3 M) in D$_2$O/H$_2$O [90%/10% (vol/vol)] with an NaH$_2$PO$_4$/Na$_2$HPO$_4$ buffer at pH 7.5–8.
ii) Sodium [1-^{13}C]-acetate (3 M) in D$_2$O/H$_2$O [90%/10% (vol/vol)].
iii) A mixture of sodium fumarate/alanine-glycine [CH$_3$CH(NH$_2$)^{13}CONHCH$_2$^{13}COOH]/sodium [1-^{13}C]-acetate (1 M/1 M-1 M) in D$_2$O/H$_2$O [90%/10% (vol/vol)].

Typically, 20 mg HYPSO materials are impregnated with 36 μL solution [*V* (microliters) = 1.8 m (milligrams)], and the wetted solid is placed in the home-built prepolarizer.

1. Gajan D, et al. (2013) Solid-phase polarization matrixes for dynamic nuclear polarization from homogeneously distributed radicals in mesostructured hybrid silica materials. *J Am Chem Soc* 135(41):15459–15466.
2. Gheorghe A, Matsuno A, Reiser O (2006) Expedient immobilization of TEMPO by copper-catalyzed azide-alkyne [3+2]-cycloaddition onto polystyrene resin. *Adv Synth Catal* 348(9):1016–1020.
3. Reddy TJ, Iwama T, Halpern HJ, Rawal VH (2002) General synthesis of persistent trityl radicals for EPR imaging of biological systems. *J Org Chem* 67(14):4635–4639.

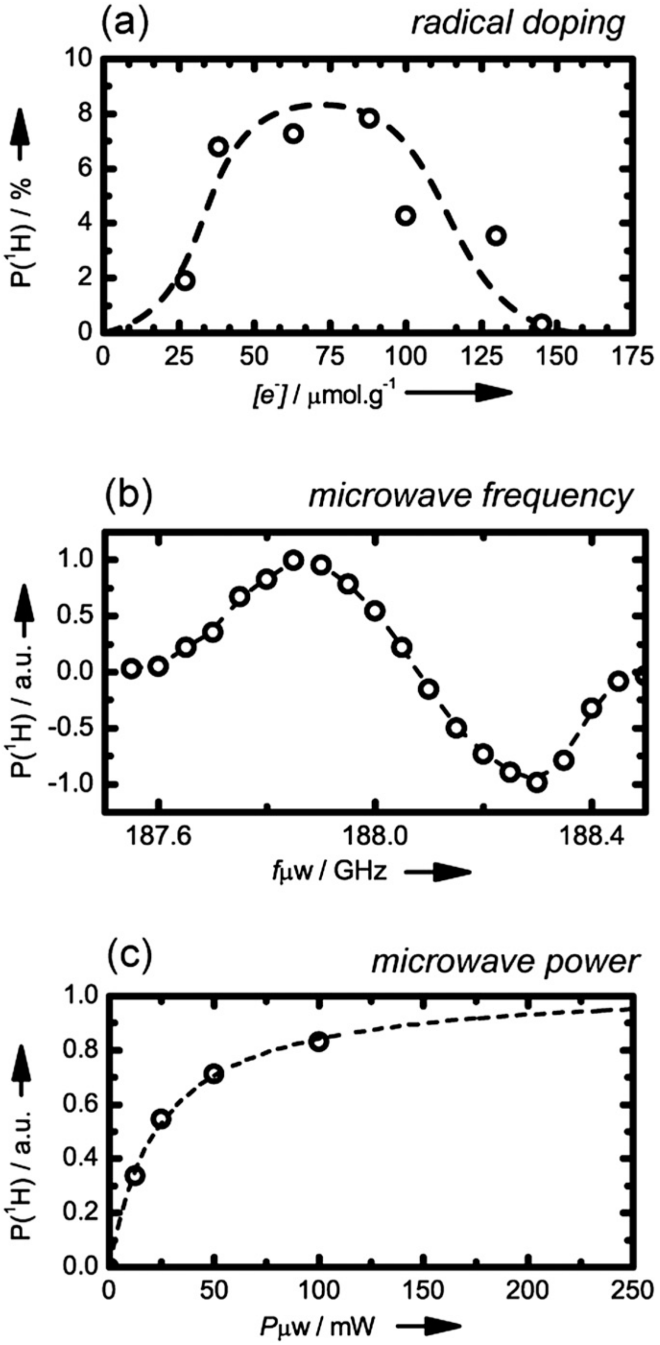

Fig. S1. (*A*) Optimization of the polarizing agent concentration in HYPSO 1.0. Maximum ^{1}H polarization was obtained in 40 μL H_2O/D_2O [10:90 (vol:vol)] mixtures in 20 mg different samples at $T = 4.2$ K and $B_0 = 6.7$ T. The optimization was performed at $T = 4.2$ K rather than $T = 1.2$ K, because the buildup times are faster. The electron concentration in the materials ranges from 25 to 140 $\mu mol \cdot g^{-1}$. The polarization achieved with HYPSO 1.0 containing 88 $\mu mol \cdot g^{-1}$ TEMPO functionalities depends on the microwave power and microwave frequency. (*B*) The dynamic nuclear polarization (DNP) as a function of microwave frequency measured at $T = 4.2$ K displays a shape similar to that typically obtained for DNP in frozen glasses without porous materials. Positive and negative extrema occur for $f_{\mu w}^{+}$ = 187.85 and 188.3 GHz, respectively. (*C*) The DNP microwave saturation curve measured at $T = 1.2$ K indicates that only 100 mW suffice to achieve at least 80% of full saturation.

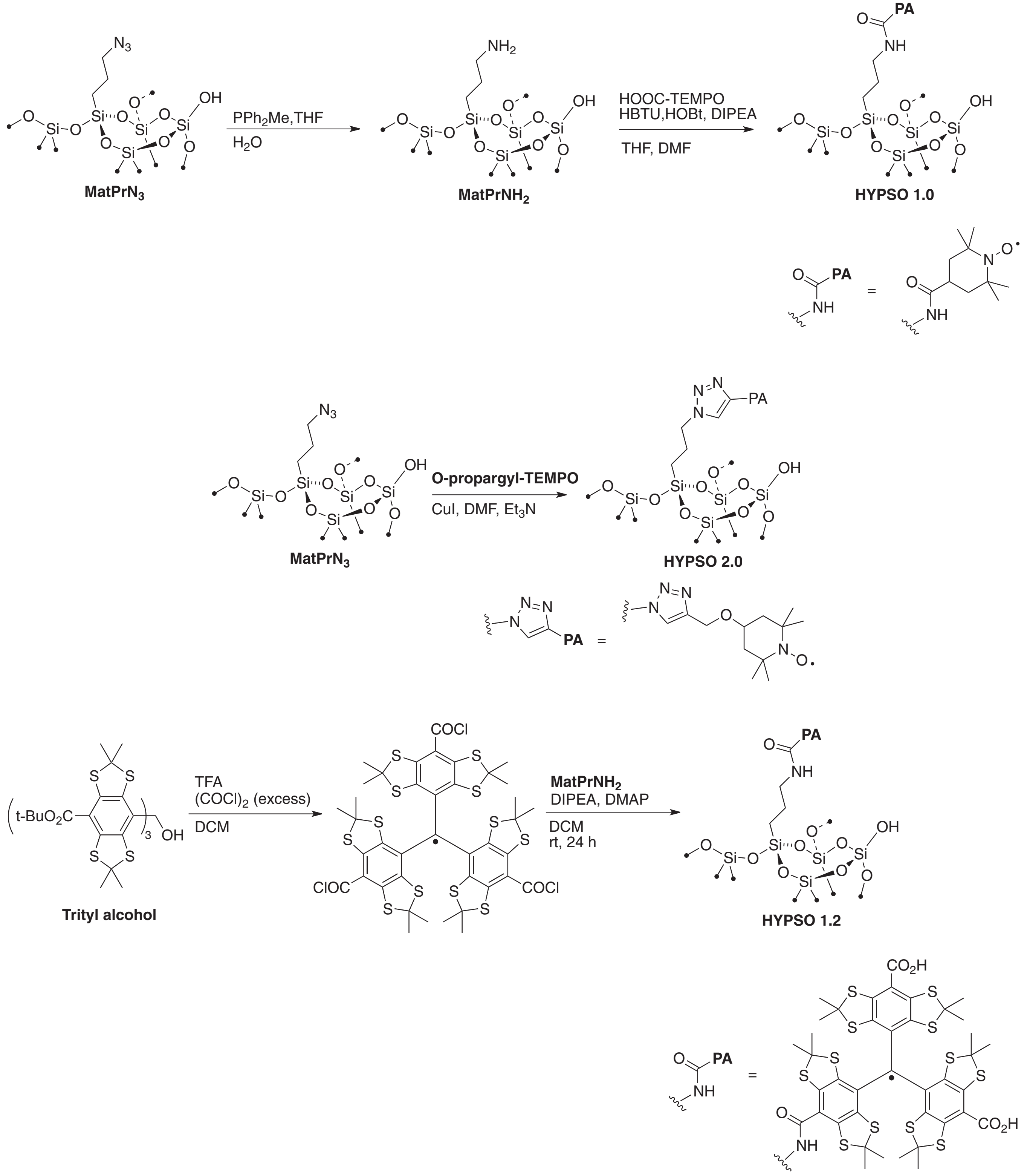

Fig. S2. Synthesis steps for the preparation of HYPSO 1.0, 2.0, and 1.2. THF, tetrahydrofuran.

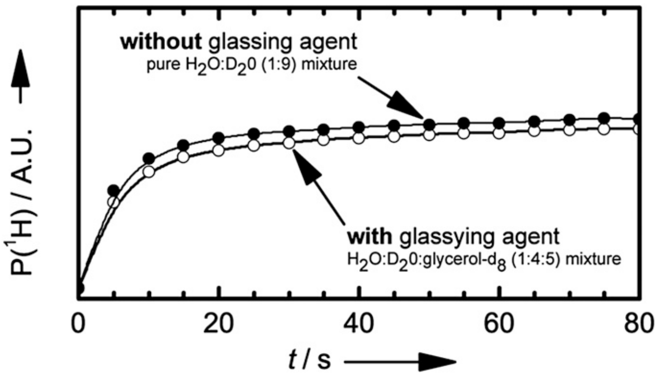

Fig. S3. Comparison between the ^{1}H dynamic nuclear polarization buildup at $T = 4.2$ K in 40 μL H_2O:D_2O mixture [10:90 (vol:vol); ●] and H_2O:D_2O:glycerol-d_8 mixture [10:40:50 (vol:vol:vol); ○] impregnated into 20 mg 88 μmol·g^{-1} HYPSO 1.0 at $T = 4.2$ K. Not only does the presence of the glass-forming agent glycerol not improve the efficiency of dynamic nuclear polarization, but it has a slightly deleterious effect.

Table S1. N_2 adsorption at 77 K and X-ray diffraction analysis

	N_2 adsorption/desorption[*]			X-ray diffraction			
Material	d_p (nm)[†]	a_s (m^2·g^{-1})[‡]	V_p (cm^3·g^{-1})[§]	Structure	d(100) (nm)	A_0 (nm)	Wall (nm)[¶]
HYPSO 1.2	10.6	647	1.17	Hexagonal	11.5	13.2	2.6
HYPSO 2.0	8.0	849	1.04	Hexagonal	10.5	12.1	4.1

[*] All materials displayed typical type IV isotherms.

[†] Mean pore diameter of mesopores calculated using Barrett–Joyner–Halenda analysis of the adsorption curve.

[‡] Surface area calculated using Brunauer–Emmet–Teller analysis.

[§] Pore volume calculated using Barrett–Joyner–Halenda analysis.

[¶] Wall thickness calculated by $A_0 - d_p$.

Table S2. EPR analysis

Material	Radical conc. (mmol g^{-1})	Line width (G)	Yield by EPR (%)
HYPSO 1.2	0.016	2.3	7
HYPSO 2.0	0.041	12.1	36