Supporting Information for

Nanoporous Metal-organic Framework as Renewable Size-selective Hydrogen-Bonding Catalyst in Water

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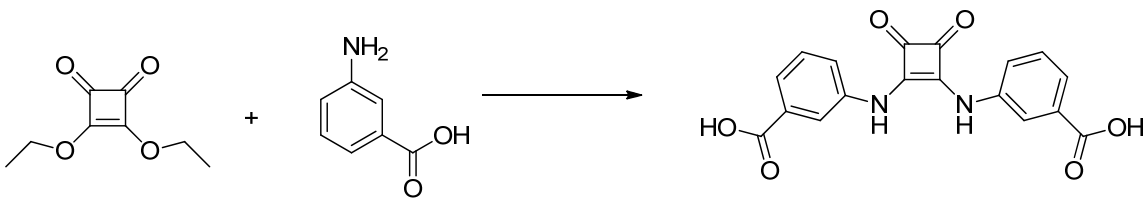
Materials and Methods.

Reagents and chemicals: All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. 3,4-diethoxy-3-cyclobutene-1,2-dione, 3-aminobenzoic acid, 1-Phenyl-1,3-butanedione, Dibenzoylmethane, Ethyl acetoacetate, 2,4-Pentanedione, Methyl acetoacetate, *tert*-Butyl acetoacetate, trans-*β*-Nitrostyrene, trans-4-Methoxy-*β*-nitrostyrene, *β*,4-Dinitrostyrene, (*E*)-1-Methyl-4-(2-nitrovinyl)benzene, trans-3-Bromo-*β*-nitrostyrene and trans-2-Bromo-*β*-nitrostyrene were purchased from Beijing Innochem Science & Technology Co.,Ltd.

Instruments and spectroscopic measurements: The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. ^{1}H NMR spectra were measured on a Bruker-400 spectrometer with Me_4Si as an internal standard. X-Ray powder diffraction (XRD) patterns of the Zn−DBDA was recorded on a Rigaku D/max-2400 X−ray powder diffractometer (Japan) using Cu−Kα (λ =1.5405 Å) radiation. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 5 °C/min in a nitrogen flow with a Mettler-Toledo TGA/SDTA851 instrument. FT-IR spectra were recorded as KBr pellets on Bruker Optics TENSOR 27 FT-IR spectrophotometer. The Zn^{2+} content before and after catalytic were measured by Inductively Coupled Plasma Spectrometer (Perkin Elmer). The solution fluorescent spectra were measured on Jasco V-530. Both excitation and emission slit widths were 2.5 nm, and fluorescence measurements were carried out in a 1 cm quartzcuvette with stirring the suspension of Zn−DBDA. Gas adsorption isotherms were obtained using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc. using the volumetric technique. For the Gaussian calculations, we used the popular B3LYP functional combined with the standard basis set 6-31G(d,p). The starting structures of Zn−DBDA is their crystallographic geometries, considering the experimental results, the Gaussian calculations are only performed for the 1:1 complexes, including the geometry optimization and vibrational spectral analysis.

Synthesis of the H_2dbda (3,3'-((3,4-dioxocyclobut-1-ene-1,2-diyl)bis(azanediyl))dibenzoic acid) ligand.



3-Aminobenzoic acid (576 mg, 4.2 mmol), $Zn(CF_3SO_3)_2$ (145 mg, 0.4 mmol), and 3,4-diethoxy-3-cyclobutene-1,2-dione (295 uL, 2 mmol) was added into 19.0 mL toluene and 1.0 mL NMP. After heating to reflux at 100 °C for 24 h under a N_2 atmosphere, a yellow precipitate was harvested by filtration and washed with MeOH (10 mL). To further purify the product, the yellow solid was stirred in boiling MeOH (20 mL) for 5 min and then isolated by vacuum filtration, and washed with MeOH (3×5 mL). This purification procedure was repeated two more times, and the product was dried at 80 °C for 12 h. Yield: 0.6 g (85%) based on 3,4-diethoxy-3-cyclobutene-1,2-dione. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.36 (s, 2H), 8.13 (s, 2H), 7.99 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 2H). ESI-MS (m/z): $[M]^-$ calculated for $[C_{18}H_{11}N_2O_6]^-$ 351.3, found 350.9.

X-ray Crystallography (Single-crystal diffraction) and Characterizations of Zn−DBDA.

Crystal data of Zn−DBDA:

$C_{33}H_{45}N_7O_{12}Zn_{1.5}$, Mr = 829.8, Monoclinic, space group *P*2(1)/*c*, a = 5.9994(12), b = 29.661(6), c = 19.068(4) Å, α = 90.00, β = 90.09, γ = 90.00, V = 3393.0(12) Å^3, Z = 4, *D*c = 1.624 g cm^{-3}, μ(Mo-Kα) = 1.146 mm^{-1}, *T* = 296(2) K. 19212 unique reflections [R_{int} = 0.1398]. Final R_1[with $I > 2\sigma(I)$] = 0.0637, wR_2(all data) = 0.1262, GOOF = 1.003. CCDC number: 1810642.

Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. In addition to the two DMF molecules that were modelled, the masking process was used and 478 electrons were found in a volume of 988 Å^3 void per unit cell. With Z = 4 in this case, this is equivalent to the removal of 478/4 = 119.5 electrons from the formula unit. This is consistent with the presence of 3[C_3H_7NO] per Formula Unit which account for 480 electrons per unit cell.

Selective bond distance (Å) and angle (°) in Zn−DBDA.

Zn(1)–O(1W)	2.04 6(3)	Zn(1)–O(1WA)	2.04 6(3)
Zn(1)–O(3B)	2.1 18(4)	Zn(1)–O(3C)	2.1 18(4)
Zn(1)–O(5A)	2.1 25(4)	Zn(1)–O(5)	2.1 25(4)
Zn(2)–O(6A)	1.9 0 5(5)	Zn(2)–O(4D)	1.9 2 5(5)

Zn(2)–O(1W)	1.9 83(3)	Zn(2)–O(1WE)	1.9 99(3)
O(1W)–Zn(1)–O(3B)	97. 11(16)	O(1WA)–Zn(1)–O(3B)	82. 89(16)
O(1W)–Zn(1)–O(3C)	82. 89(17)	O(1WA)–Zn(1)–O(3C)	97. 11(16)
O(3B)–Zn(1)–O(3C)	180.00(13)	O(1W)–Zn(1)–O(5A)	96. 53(16)
O(1WA)–Zn(1)–O(5A)	83. 47(16)	O(3B)–Zn(1)–O(5A)	89. 59(19)
O(3C)–Zn(1)–O(5A)	90. 41(19)	O(1W)–Zn(1)–O(5)	83. 47(16)
O(1WA)–Zn(1)–O(5)	96. 53(16)	O(3B)–Zn(1)–O(5)	90. 41(19)
O(3C)–Zn(1)–O(5)	89. 59(19)	O(5A)–Zn(1)–O(5)	180.0
O(6A)–Zn(2)–O(4D)	107. 6(2)	O(6A)–Zn(2)–O(1W)	118. 26(18)
O(4D)–Zn(2)–O(1W)	117. 80(18)	O(6A)–Zn(2)–O(1WA)	109. 44(18)
O(4D)–Zn(2)–O(1WE)	116. 41(18)	O(1W)–Zn(2)–O(1WE)	86.07(12)
O(1WA)–Zn(1)–O(1W)	180.0		

Symmetry code A: 2-*x*, 1-*y*, 1-*z*; B: 3-*x*, -0.5+*y*, 1.5-*z*; C: -1+x, 1.5-y, -0.5+z; D: 2-x, -0.5+y, 1.5-z; E: 1-x, 1-y, 1-z.

Figure S1 The coordination environment of Zn(II) in Zn−DBDA.

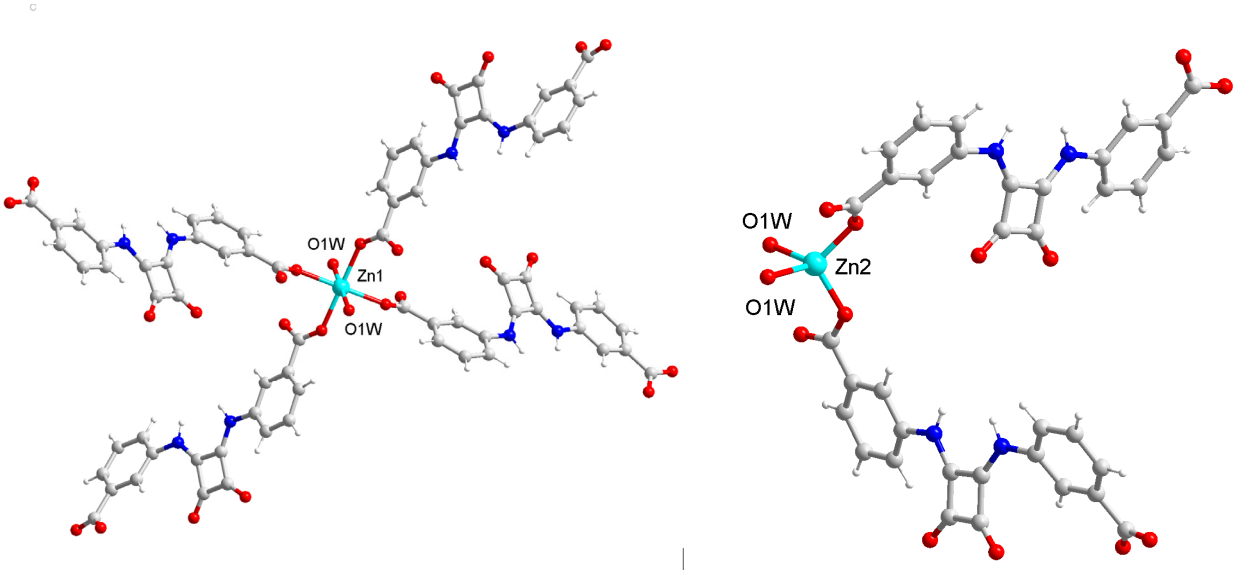


Figure S2 The coordination mode of $dbda^{2-}$ ligands in Zn−DBDA.

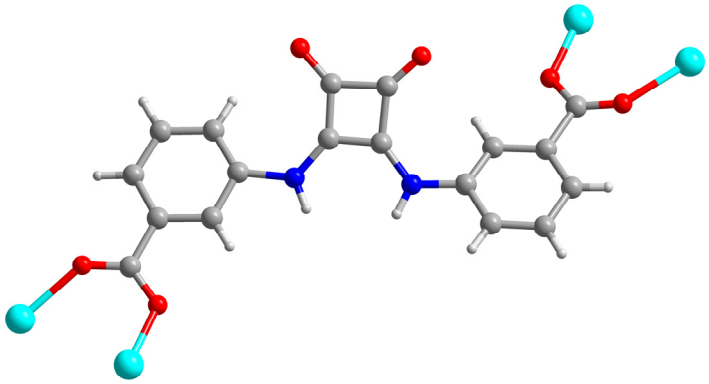


Figure S3 CO_2 adsorption/desorption isotherms of Zn−DBDA at 195 K.

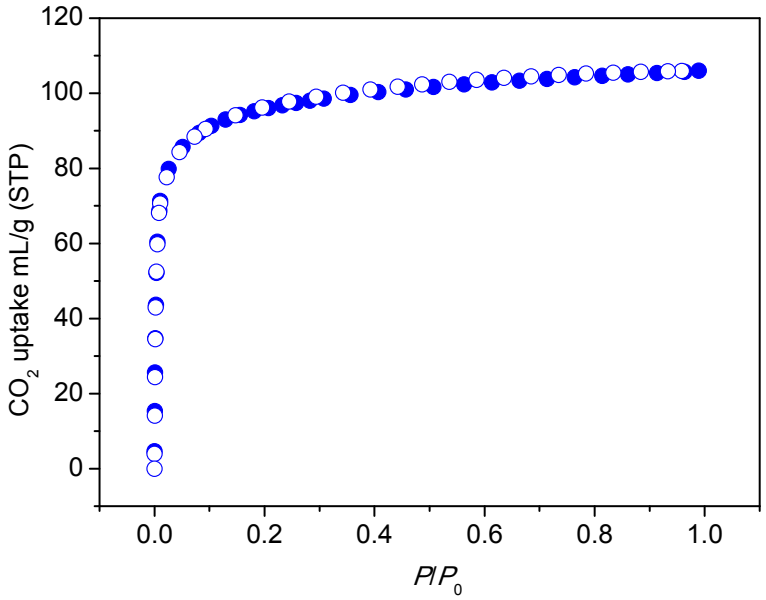


Figure S4 TGA traces of Zn−DBDA ranging from room temperature to 600 °C.

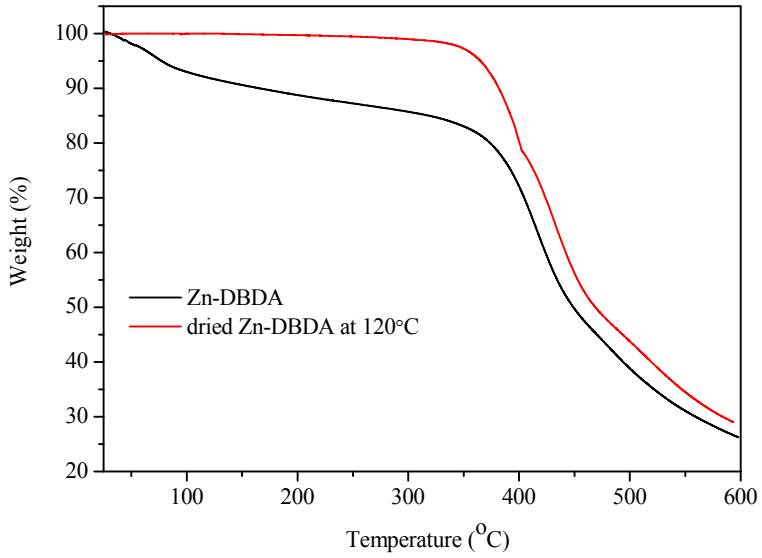


Figure S5 Powder XRD patterns of Zn−DBDA simulated from single-crystal X-ray diffraction results, the as-synthesized Zn−DBDA and Zn−DBDA treated with water.

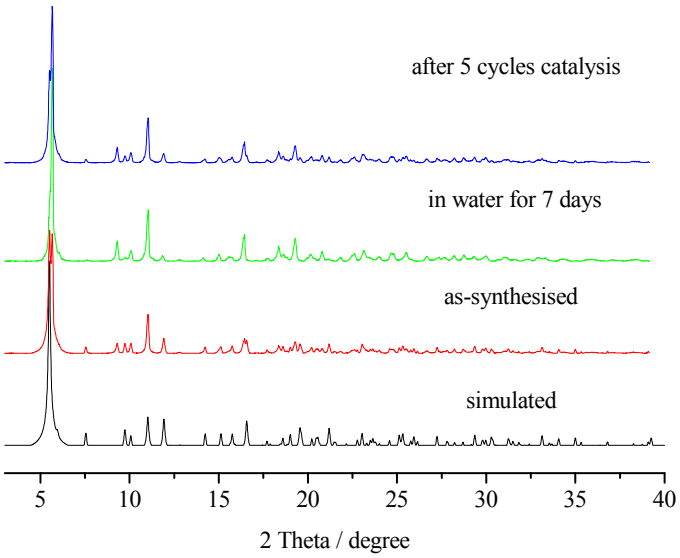


Figure S6 Family of fluorescence spectra of Zn−DBDA (0.55 mM) upon addition of *β*-nitrostyrene up to 0.23 mM; and the Stern−Volmer plot of Zn−DBDA quenched by *β*-nitrostyrene, where I_0 and I are the fluorescence intensity ratio before and after *β*-nitrostyrene incorporation, respectively.

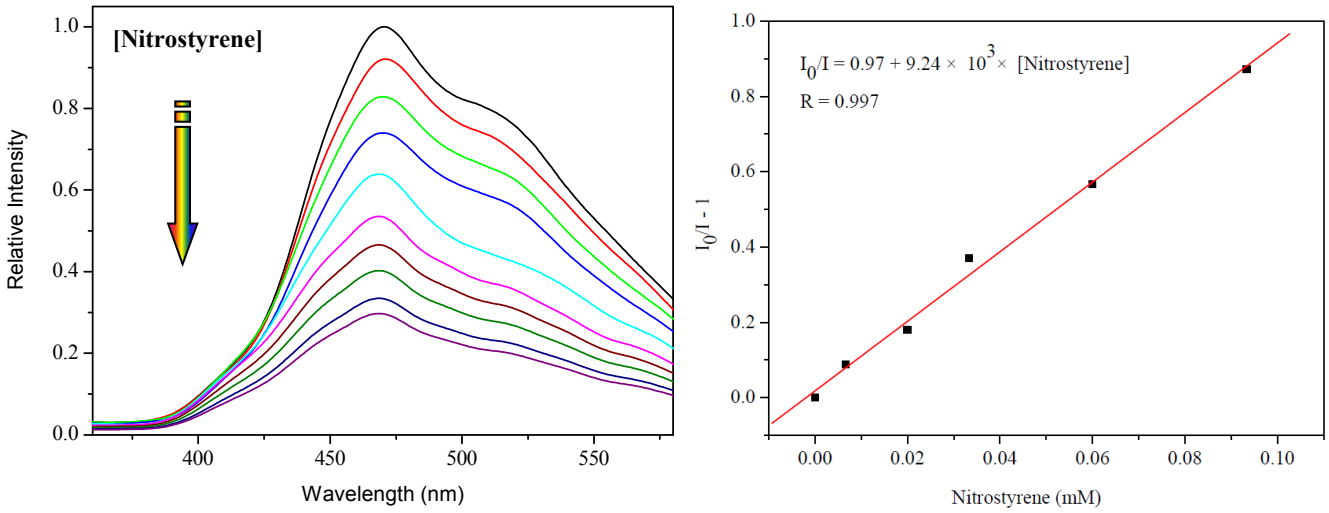


Figure S7 Family of fluorescence spectra of Zn−DBDA (0.55 mM) upon addition of Hacac up to 1.5 mM; and the Stern−Volmer plot of Zn−DBDA quenched by Hacac, where I_0 and I are the fluorescence intensity ratio before and after Hacac incorporation, respectively.

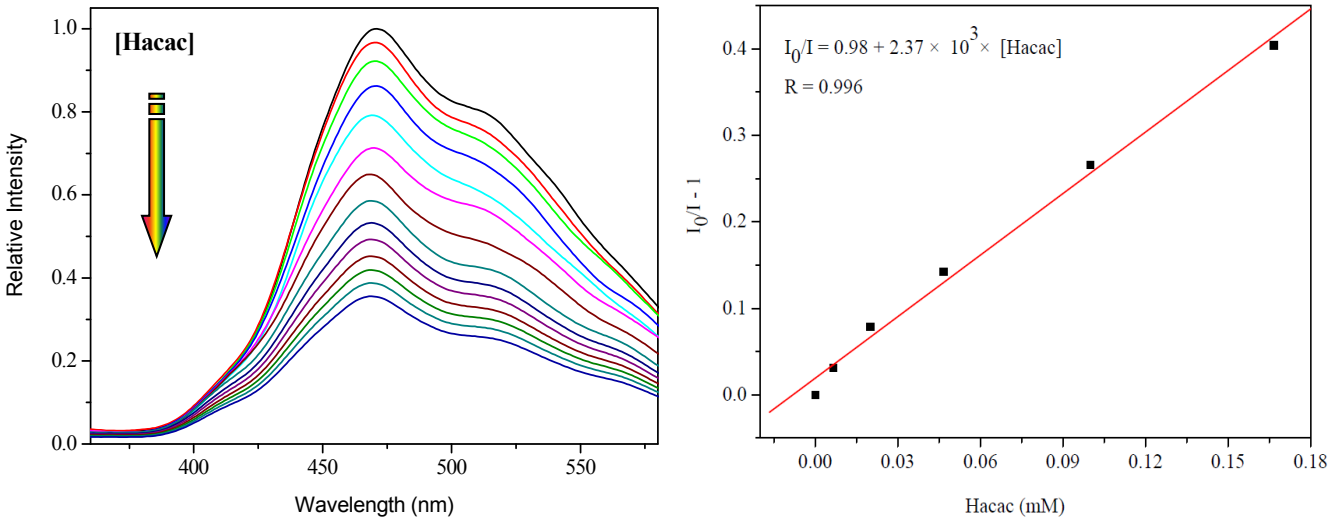


Figure S8 FT-IR spectra of Zn–DBDA (top), Zn–DBDA obtained after the absorption of *β*-nitrostyrene (middle) and *β*-nitrostyrene itself (bottom).

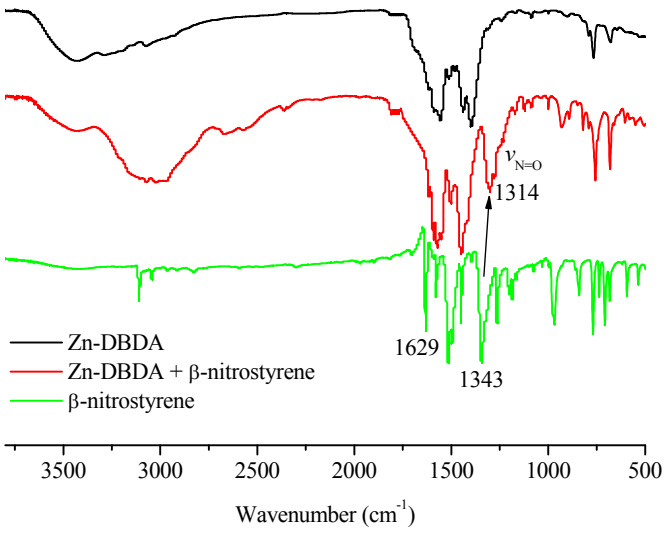


Figure S9 FT-IR spectra of Zn–DBDA (top), Zn–DBDA obtained after the absorption of Hacac (middle) and Hacac itself (bottom).

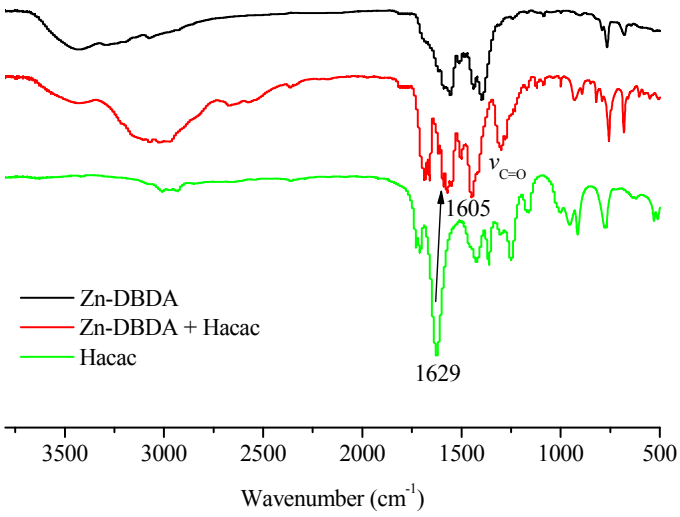


Figure S10 The ^{1}H-NMR spectra of the Zn–DBDA after β-nitrostyrene adsorption (decomposed by DCl).

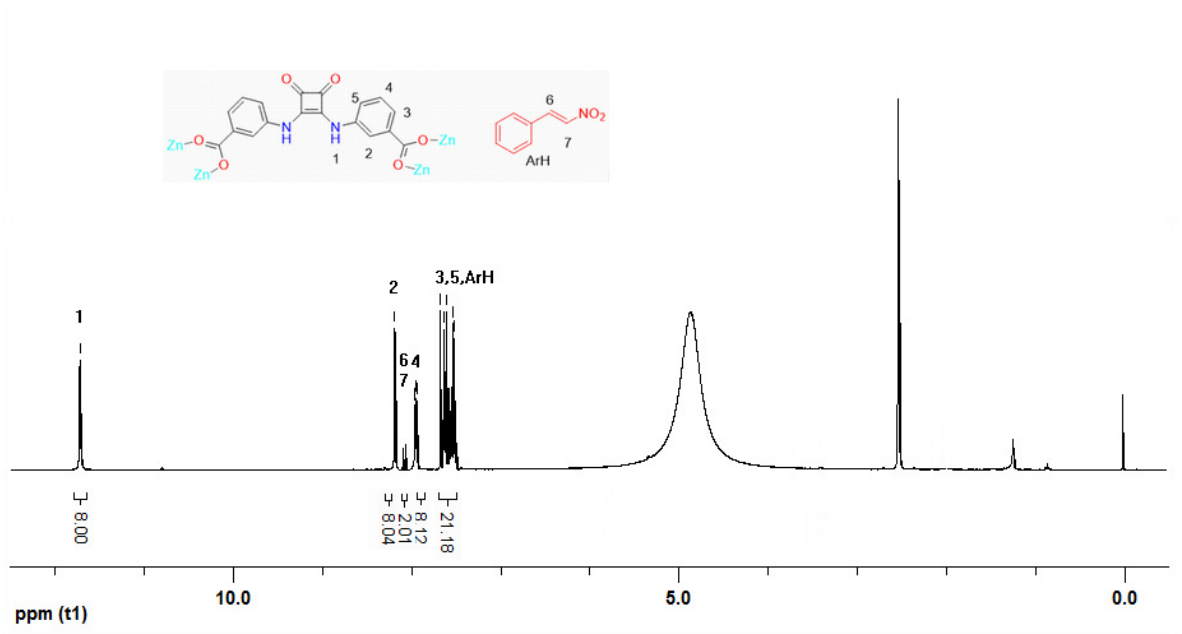


Figure S11 The ^{1}H-NMR spectra of the Zn–DBDA after Hacac adsorption (decomposed by DCl).

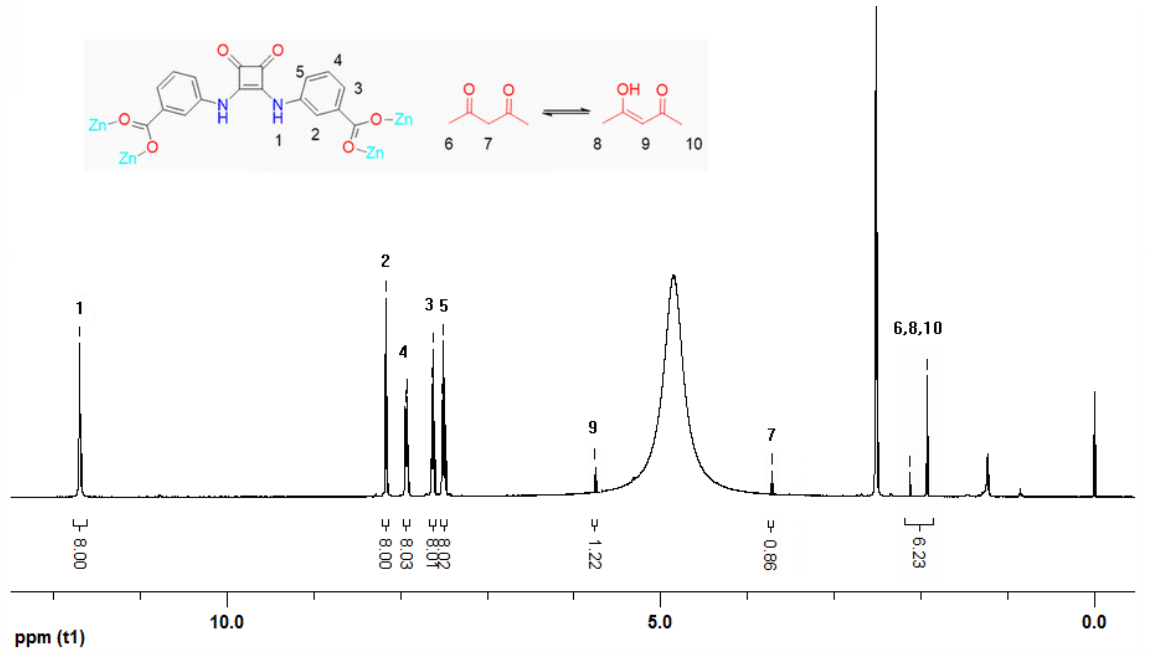


Figure S12 Yields of 3-(2-nitro-1-phenylethyl)pentane-2,4-dione catalyzed by Zn–DBDA (violet) and without Zn–DBDA through filtration after 2 hrs of the reaction (green).

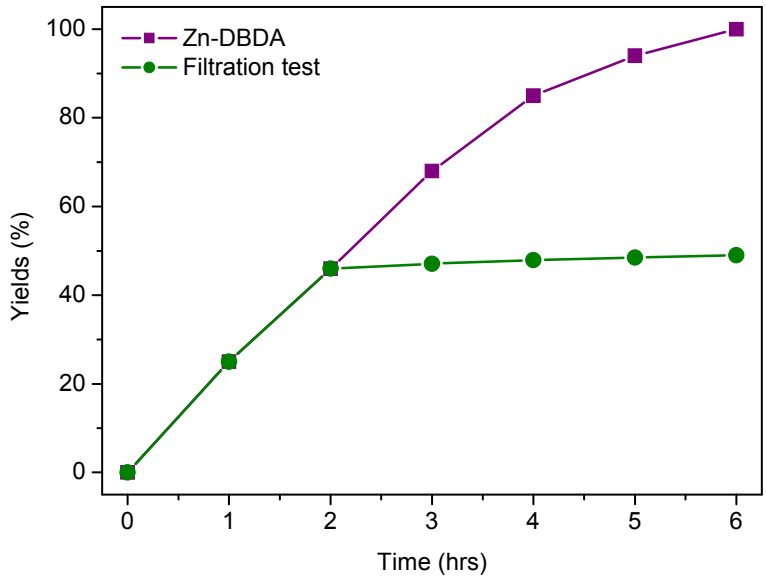


Figure S13 Study on recycling of catalyst Zn–DBDA for the heterogeneous Michael addition of acetylacetone with β-nitrostyrene.