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Supporting Information for

Interception Copper-based Carbene Radical with α-Carbonyl Diazomethane Radical: C1/C1N2 Copolymerization

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Methods

Materials

All experiments were carried out in distilled solvents under dry nitrogen atmosphere. The solvents were purchased from Sinopharm Chemical Reagent Co. Ltd and distilled before use. 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO, 98%, Aldrich), *N-tert*-butyl-α-phenylnitrone (PBN, 98%, Aldrich) and 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO, 98%, Adamas Reagent Co. Ltd) were stored at -20 °C and used as received.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Mecury VX-300 spectrometer (300 MHz) using $CDCl_3$ as solvent and trimethylsilane (TMS) as the internal standard.

The number-average molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) of the polymer samples were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards in THF solution (1.0 mL min^{-1}) at 30 ^{o}C and GPC is equipped with a Waters 717 plus auto sampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Shodex K-805, K-804, and K-802.5 columns in series.

Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometric analyses were performed on Shimadzu Biotech Axima TOF spectrometer.

Elemental analysis (EA) data were collected using a Vario EL instrument.

Online infrared (IR) spectra were collected on an is10 (Thermo) with a fiber optical system (MultiLoop-MIR) designed for infrared sampling of liquids (detection range: 1600-3400 cm^{-1}).

Ultraviolet-visible (UV-vis) spectra were recorded on an UV-3600 (Shimadzu) equipment.

Steady-state fluorescence spectra were recorded on RF-5301PC (Shimadzu).

FT-IR spectra were recorded on a Thermo is10 spectrometer.

Raman spectra were recorded on an RM-1000 confocal Raman microscope (Renishaw) with an excitation wavelength of 514.5 nm using an Ar^{+} laser.

X-ray photoelectron spectroscopic (XPS) measurements were performed on an X-ray photoelectron spectroscopy (XSAM800, Kratos, UK).

Scanning electron microscopy (SEM) observation was done by a Sirion 200 field emission scanning electron microscope (FEI Co., Eindhoven).

Energy dispersive X-ray spectroscopy (EDS) spectra were recorded by JEM-2100 (HR) using nickel screen as sample carriers.

Differential scanning calorimetry (DSC) was performed on a Q20 (TA) instrument with nitrogen as the protecting gas.

Thermo gravimetric analysis (TGA) was measured with a NETZSCHSTA 449C thermal analyzer (NETZSCHSTA, Germany) with nitrogen as the protecting gas. The oligomer was heated with a rate of 20 ^{o}C / min.

X-band Electron paramagnetic resonance (EPR) spectra were recorded on Bruker Biospin A200 spectrometer. Conditions: Sweep Width: 100.00 G; Microwave Frequency: 9.417 GHz; Microwave Power: 19.510 mW; Modulation amplitude of 1.00 G; Modulation Frequency: 100.00 kHz. The spectra were simulated by iteration of the anisotropic g-values, hyperfine coupling constants, and line widths using Biomolecular EPR Spectroscopy Software developed by W. R. Hagen.

Geometry of all systems was optimized by BP86 density functional method in combination with

def2-SVP basis-set. When evaluating single-point energies, the basis-set used was upgraded to def2-TZVP. ORCA 3.0.3 program was used to conduct the calculations. In order to evaluate the distribution of the unpaired electron and thus examine the radical site, Multiwfn 3.3.7 program was employed to calculate spin density and obtain spin population via Mulliken method.

Preparation of poly(imidazole-Cu) catalyst

The poly(imidazole-Cu) was prepared by self-assembly of $CuSO_4$ and amphiphilic poly[(*N*-vinylimidazole)-*co*-(*N*-isopropylacrylamide)] in $CHCl_3/H_2O$ solution *via* coordinative convolution method at 70 °C. The SEM image reveals poly(imidazole-Cu) formed blocky-aggregated structure and the EDS analysis confirms the existence of the copper species (Figure S1).

Poly(imidazole-Cu)-catalyzed decomposition of EDA

A solution of toluene or $CHCl_3$ (10 ml), and poly(imidazole-Cu) catalyst (50 mg) was stirred under argon atmosphere at predetermined temperature for 30 min and then EDA (1 ml, 9.45 mmol) was introduced to the system. After 17 hours of reaction, the heterogeneous catalysts were isolated and the filtrates were concentrated to precipitate from petroleum ether to give atactic copolymers as yellow products (Table S1).

Tracing the reaction process of poly(imidazole-Cu)-mediated decomposition of EDA using online IR spectroscopy

A solution of toluene (10 ml), poly(imidazole-Cu) catalysts (30 mg) was stirred under argon for 10 min at pre-determined temperature and then EDA (300 mg, 2.63 mmol) was introduced to the system to start the polymerization reaction as well as the data collection.

The effects of TEMPO on the reaction process of poly(imidazole-Cu)-mediated decomposition of EDA

A solution of toluene (10 ml), TEMPO (0.1 g, 0.64 mmol) and poly(imidazole-Cu) (50 mg) was stirred under argon at 60 °C for 5 min and then EDA (300 mg, 2.63 mmol) was introduced to the system. The disappearance of the 2110 cm^{-1} stretching band was followed continuously to depict the decomposition dynamics of EDA in the presence of TEMPO.

Spin-trapping of radical intermediates using PBN and DMPO as spin trap

A solution of toluene (5 ml), PBN (10 mg) or DMPO (10 μL) and metal catalysts (30 mg) were stirred under argon at 60 °C for 5 min, after strict extrusion of O_2 by freeze-pump-thaw cycles, EDA (500 μL, 4.73 mmol) was introduced to the systems. Then 2 μL of the solution was collected and detected by room-temperature EPR.

Cell imaging

Hela cervical carcinoma cells and Cos7 monkey kidney fibroblast cells were incubated in Dulbecco's Modified Eagle's Medium (DMEM) supplemented with 10% fetal bovine serum (FBS) and 1% antibiotics with 5% CO_2 at 37 °C. Cells were seeded in a 6-well plate at a density of 10^5 cells per well and cultured in 1 mL DMEM with 10% FBS for 24 h. Then, a solution of the copolymer (500 μg) dissolved in 1 mL DMEM with the addition of 10% FBS, 1% antibiotics and 5% DMSO and further incubated for another 4 h at 37 °C. The cells were washed twice with 1 mL

PBS upon removing the medium. The fluorescence imaging was acquired with confocal laser scanning microscopy (CLSM) equipped with the excitation filter (405/40 nm) and emission filter (535/50 nm).

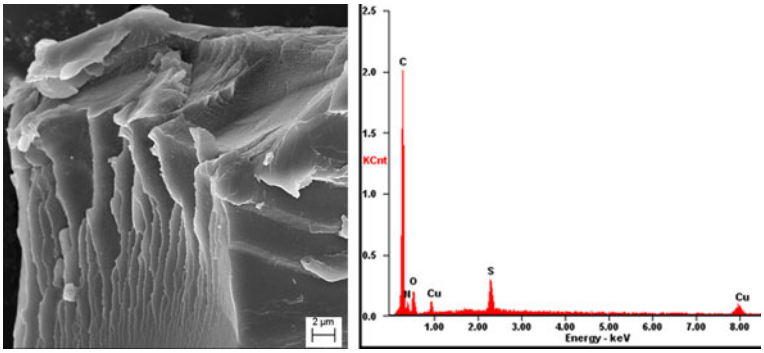

Fig. S1 SEM and EDS images of poly(imidazole-Cu).

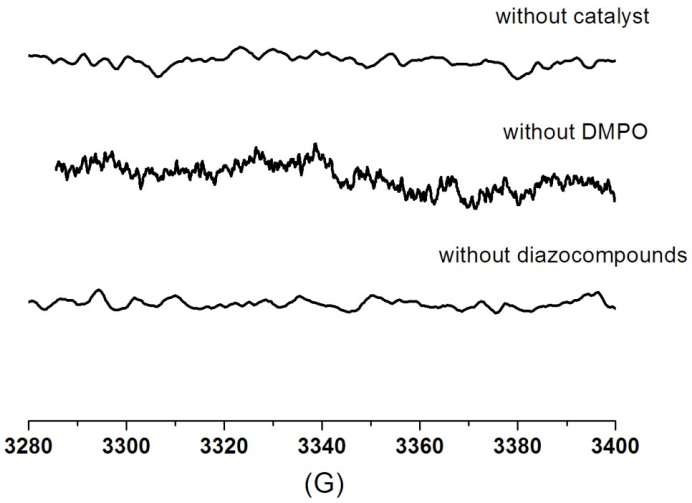

Fig. S2 Control experiments suggest that in the absence of metal catalysts, EDA or DMPO, no EPR signals could be detected, which in turn confirms that the radicals were generated during the interaction of the metal-catalysts and the diazocompounds.

Scheme S1 Poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA

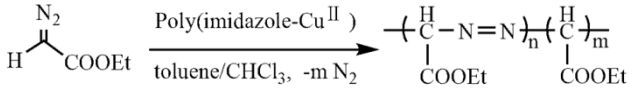

Table S1 Poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA[a]

Entry	solvent	Temperature (°C)	yield (%)[b]	M_n[c] (g mol^{-1})	M_w/M_n[c]	elemental analysis (found)
1	toluene	30	71.74	410	1.19	N, 4.05; C, 49.06; H, 6.07
2	toluene	45	59.31	488	1.03	N, 4.39; C, 51.34; H, 6.33
3	toluene	60	53.67	684	1.15	N, 4.60; C, 51.22; H, 6.37
4	toluene	70	46.45	708	1.15	N, 8.53; C, 53.04; H, 8.05
5	toluene	100	30.64	786	1.17.	N, 5.60; C, 51.96; H, 5.97
6	$CHCl_3$	60	38.40	500	1.01	N, 9.16; C, 52.80; H, 7.57

[a] Experimental conditions: 50 mg poly(imidazole-Cu), 1 ml EDA, 10 ml solvent. [b] Yield=[the weight of copolymer]/[the weight of monomer]*100%. [c] M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF.

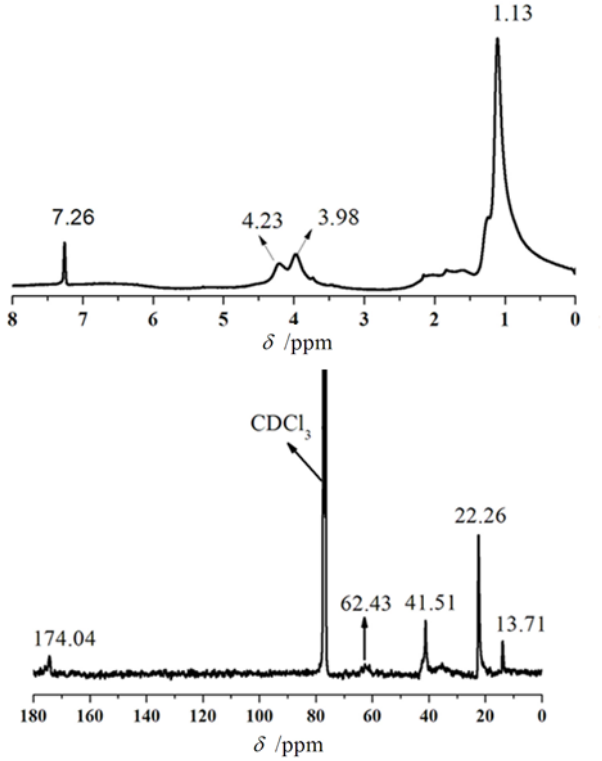

Fig. S3 ^{1}H and ^{13}C NMR spectra of the copolymer obtained with poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA.

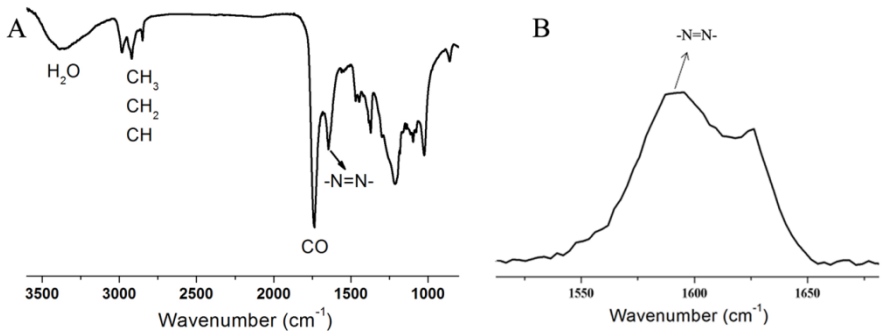

Fig. S4 FT-IR (A) and Raman spectra of the copolymer obtained with poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA.

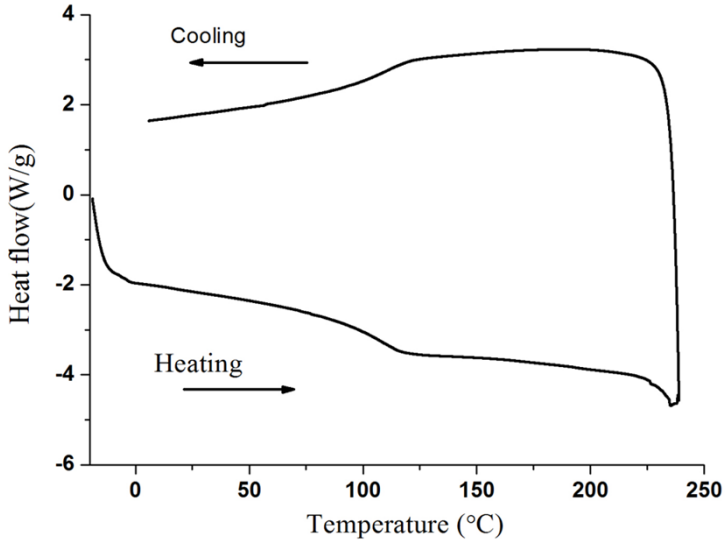

Fig. S5 DSC heating and cooling curve of amorphous copolymer obtained with poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA.

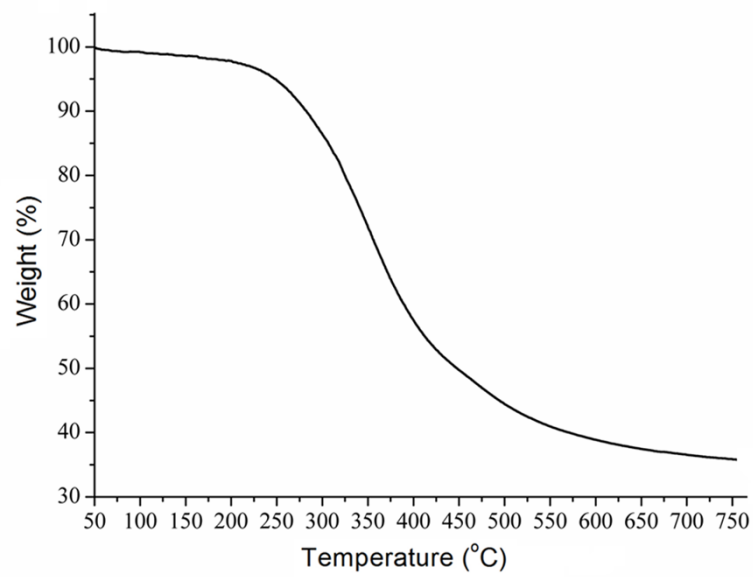

Fig. S6 TGA curve of the obtained copolymer with poly(imidazole-Cu)-mediated C1/C1N2 copolymerization of EDA.

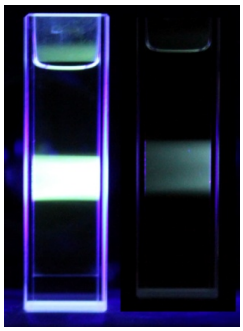

Fig. S7 Fluorescence photograph of copolymer taken under 448 nm (left) and 844 nm (right) excitation light ($CHCl_3$ as solvent).

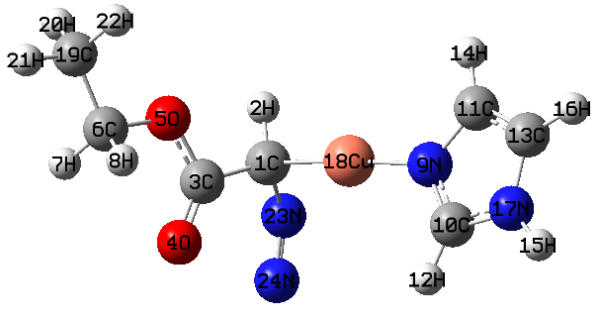

Fig. S8 Molecular structure of copper-dizao radical optimized by BP86 density functional method.

Population of atoms:

Atom	Alpha_pop.	Beta_pop.	Spin_pop.	Atomic charge
1(C)	3.12864	3.02415	0.10449	-0.15279
2(H)	0.48522	0.48912	-0.00390	0.02566
3(C)	2.93066	2.90901	0.02165	0.16032
4(O)	4.11386	4.10361	0.01025	-0.21746

5(O)	4.15314	4.14641	0.00673	-0.29955
6(C)	2.94044	2.93597	0.00447	0.12359
7(H)	0.48239	0.48247	-0.00008	0.03514
8(H)	0.48868	0.48826	0.00042	0.02306
9(N)	3.62354	3.62276	0.00078	-0.24629
10(C)	2.93540	2.92781	0.00760	0.13679
11(C)	2.97463	2.97386	0.00077	0.05151
12(H)	0.45881	0.45925	-0.00045	0.08194
13(C)	2.99000	2.99084	-0.00084	0.01917
14(H)	0.47369	0.47383	-0.00014	0.05248
15(H)	0.41807	0.41799	0.00009	0.16394
16(H)	0.47349	0.47341	0.00009	0.05310
17(N)	3.53892	3.53763	0.00129	-0.07656
18(Cu)	14.38501	14.37044	0.01456	0.24455
19(C)	3.03262	3.03282	-0.00020	-0.06544
20(H)	0.47861	0.47858	0.00003	0.04280
21(H)	0.48494	0.48436	0.00057	0.03070
22(H)	0.48204	0.48204	-0.00001	0.03592
23(N)	3.62045	3.44898	0.17147	-0.06943
24(N)	3.90675	3.24640	0.66036	-0.15315
Total net charge:	0.00000	Total spin electrons:	1.00000	

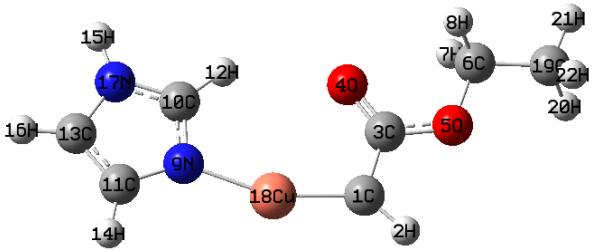

Fig. S9 Molecular structure of copper-carbene radical optimized by BP86 density functional method.

Population of atoms:

Atom	Alpha_pop.	Beta_pop.	Spin_pop.	Atomic	charge
1(C)	3.53575	2.75438	0.78137	-0.29013	
2(H)	0.48281	0.51717	-0.03436	0.00003	
3(C)	2.88192	2.90451	-0.02260	0.21357	
4(O)	4.22174	4.06549	0.15625	-0.28723	
5(O)	4.16415	4.12281	0.04134	-0.28695	
6(C)	2.93633	2.93914	-0.00281	0.12453	
7(H)	0.49001	0.48696	0.00304	0.02303	
8(H)	0.49001	0.48696	0.00304	0.02303	
9(N)	3.62001	3.62565	-0.00564	-0.24567	

	10(C)	2.93521	2.92438	0.01083	0.14041
	11(C)	2.98199	2.97832	0.00368	0.03969
	12(H)	0.45446	0.45572	-0.00125	0.08982
	13(C)	2.99418	2.99529	-0.00111	0.01053
	14(H)	0.47788	0.47814	-0.00026	0.04397
	15(H)	0.41962	0.41973	-0.00011	0.16065
	16(H)	0.47700	0.47706	-0.00006	0.04595
	17(N)	3.53521	3.53404	0.00117	-0.06925
	18(Cu)	14.42271	14.35547	0.06724	0.22182
	19(C)	3.03297	3.03300	-0.00003	-0.06597
	20(H)	0.47988	0.47968	0.00021	0.04044
	21(H)	0.48628	0.48644	-0.00015	0.02728
	22(H)	0.47988	0.47968	0.00021	0.04044
Total	Net charge: -0.00000			Total spin electrons: 1.00000	