Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

A functional triazine framework based on N-heterocyclic building blocks

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1. Experimental

1.1. Materials

Table S1. List of used materials with supplier, purity, and purification information.

Chemical	Molecular Formula	Supplier	Purity	Purification
Bis(dibenzylideneacetone)palladium(0)	$C_{34}H_{28}O_2Pd$	Sigma-Aldrich	-	-
1,5-Bis(diphenylphosphino)pentane	$C_{29}H_{30}P_2$	Alfa Aesar	97%	-
5-Bromo-2-idopyridine	C_5H_3BrI	Alfa Aesar	98%	-
Cobalt(II) chloride hexahydrate	$Cl_2Co \cdot 6H_2O$	AppliChem	97%	-
1,2-Dibromoethane	$C_2H_4Br_2$	Fluka	98%	-
Dimethylformamide	C_3H_7NO	Alfa Aesar	99%	-
Lithium chloride	ClLi	Grüssing	99%	-
Magnesium	Mg	Grüssing	99%	-
Nickel(II) chloride hexahydrate	$Cl_2Ni \cdot 6H_2O$	Grüssing	98%	-
Potassium tetrachloro platinate(II)	Cl_4K_2Pt	Alfa Aesar	99.9%	-
Sodium tetrachloropalladate(II) trihydrate	$Cl_4Na_2Pd \cdot 3H_2O$	Strem Chemicals	99%	-
Tetrahydrofuran	C_4H_8O	BASF	-	Predried over CaH_2 and refluxed over Na, Benzophenon ketyl
Trimethylsilyl chloride	C_3H_9ClSi	Sigma-Aldrich	98%	-
Zinc chloride	Cl_2Zn	BDH Prolabo	98%	6h, 140 °C, HV
Zinc cyanide	C_2N_2Zn	ABCR	98%	-

1.2. Temperature programs

Table S2. Temperature programs for the *bipy*-CTF synthesis.

Program	Sample	Heating rate [°C h^{-1}]	*T*1 [°C]	Holding time *T*1 [h]	*T*2 [°C]	Holding time *T*2 [h]	Cooling rate [°C h^{-1}] [a]
1	1,2,3,4	60	375	48	-	-	10
2	5,6,7,8	60	400	48	-	-	10
3	9	60	450	48	-	-	10
4	10	60	500	48	-	-	10
5	11	60	600	48	-	-	10
6	12	60	700	48	-	-	10
7	13	60	400	40	600	0.2	10
8	14	60	400	40	600	20	10
9	15	60	400	40	600	40	10
10	16	60	400	40	600	80	10

[a] At 240 °C the oven was turned off.

1.3. Elemental analysis

Table S3. Elemental composition of *bipy*-CTF materials synthesized under different reaction conditions (in wt%). The assignments are given in Table S1.

Sample	N	C	H
calc.	27.17	69.90	2.93
5	23.09	67.06	3.01
9	20.50	65.78	3.11
10	16.95	64.14	1.81
11	13.48	75.24	1.66
12	7.61	82.44	1.44
13	17.75	71.28	1.74
14	15.59	72.57	1.62
15	14.67	74.94	0.74
16	14.33	75.41	1.48

1.4. Metal doping

Table S4. Metal uptake by different *bipy*-CTFs in wt% and mol%.

Metal	CTF	Uptake [wt%]	Uptake [mol%] [a]	Metal	CTF	Uptake [wt%]	Uptake [mol%] [a]
Pt	400	10.2	12.5	Pd	400	15.2	39.4
Pt	400	10.1	12.4	Pd	400	11.9	28.8
Pt	400	11.8	14.9	Pd	400	12.1	29.4
Pt	400	15.3	20.4	Pd	500	30.3	118.6
Pt	500	37.8	82.5	Pd	500	28.9	108.0
Pt	500	34.7	69.6	Pd	500	33.2	144.0
Pt	600	35.8	73.9	Pd	600	25.2	84.2
Pt	600	31.4	58.0	Pd	600	29.0	108.7
Pt	700	28.4	49.0	Pd	700	24.9	82.5
				Pd	700	25.9	88.3
Co	400	0.5	1.8				
Co	400	1.8	6.6	Ni	400	1.8	6.6
Co	500	2.6	9.7	Ni	400	3.1	11.7
Co	400/600	2.5	9.2	Ni	500	3.0	11.3
				Ni	400/600	3.1	11.9

[a] Mol% calculated by assumption that metal salts are adsorbed as M(II)Cl_2.

2. Characterization

2.1. Methods

Nitrogen and Argon adsorption/desorption measurements were performed at 77 K (87 K for Ar) with an Autosorb iQ instrument (Quantachrome Instruments, Boynton Beach, Florida, USA). Samples were outgassed in vacuum at 300 °C. The analysis station was equipped with high-precision pressure transducers and a turbo molecular pump. Pore-size distribution was determined using the calculation model "N_2 at 77 K on carbon" (slit-/cylinder pores, non-local DFT (equilibrium model)) of the ASiQwin software (version 1.11) by Quantachrome. For BET calculations pressure ranges were chosen with the help of the BET Assistant in the ASiQwin software (version 2.0). In accordance with the ISO recommendations multipoint BET tags equal or below the maximum in $V \cdot (1 - P/P_0)$ were chosen.

Infrared (IR) spectroscopy measurements were carried out on a Perkin Elmer Spektrum BX II (Perkin Elmer, Waltham, Massachusetts, USA) with an attenuated total reflectance unit.

Powder X-ray diffraction (XRD) was measured on a BRUKER D8 Avance (Bruker AXS, Madison, Wisconsin, USA) in Bragg-Brentano geometry or on a HUBER G670 (HUBER Diffraktionstechnik, Rimsting, Germany) in Guinier geometry equipped with an imaging plate detector.

Elemental analysis (EA) was carried out with an Elementar vario EL (Elementar Analysensysteme, Hanau, Germany).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was done on a VARIAN VISTA RL simultaneous spectrometer (Agilent Technologies, Santa Clara, California, USA) with a CCD-detector.

Solution-state NMR spectroscopy was performed on a JEOL DELTA NMR (JEOL, Tokyo, Japan) by single pulse experiments. The spectra were referenced against $CDCl_3$ ($\delta(^1H)$ 7.26 ppm, $\delta(^{13}C\{^1H\})$ 77.16 ppm).

Magic angle spinning (MAS) solid-state nuclear magnetic resonance (ssNMR) spectroscopy measurements were carried out on a BRUKER DSX500 Avance spectrometer (Bruker AXS, Madison, Wisconsin, USA) with a proton resonance frequency of 500 MHz using a 4 mm MAS-rotor (ZrO_2) in a 11.75 T magnet field with a spinning frequency of 10 kHz.

Differential thermal analysis and thermogravimetry (DTA/TG) were measured on a SETARAM TG-DTA92-2400 combined DTA-TG-thermobalance (SETARAM Instrumentation, Caluire, France) in aluminum oxide crucibles. Heating was performed from room temperature to 1000 °C with a heating rate of 5 °C min^{-1} under helium atmosphere.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed using either a JEOL JSM-6500F electron microscope (JEOL, Tokyo, Japan) with a field emission source equipped with an EDX detector model 7418 (Oxford Instruments, Oxfordshire, UK), or a Tescan Vega TS 5130MM electron microscope equipped with an Si/Li EDX detector (Oxford Instruments).

Transmission electron microscopy (TEM) was carried out on a Philips CM30 ST, 300 kV S/TEM (FEI, Hilsboro, Oregon, USA) with an Si/Li EDX-detector from Thermo Fischer, NSS.

2.2. Sorption measurements

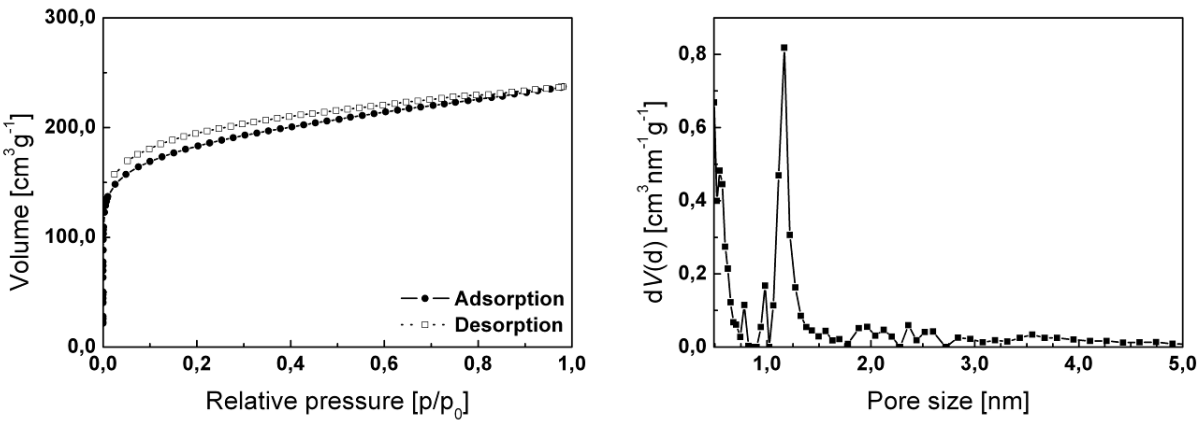


Figure S1. N_2 physisorption isotherm (left) and pore size distribution (right) of *bipy*-CTF-400 with 671 m^2 g^{-1} surface area.

2.3. X-ray powder diffraction

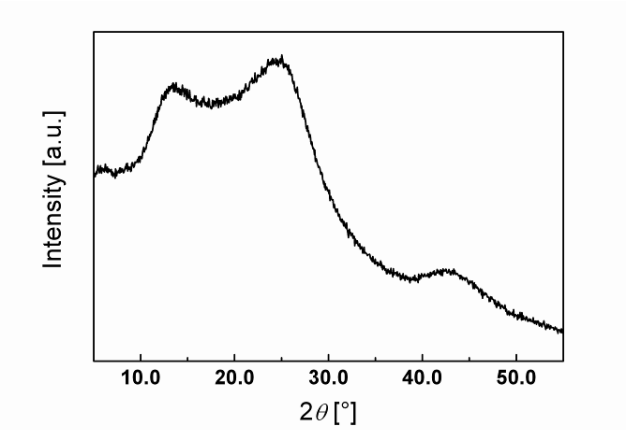


Figure S2. X-Ray powder pattern of *bipy*-CTF-400 (recorded on BRUKER D8).

2.4. Solid-state MAS NMR spectroscopy

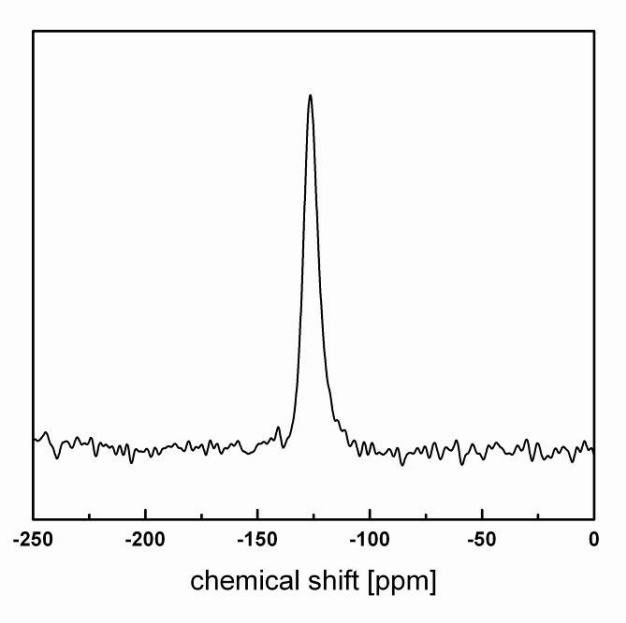


Figure S3. ^{15}N solid-state MAS NMR spectrum of CTF-1.

2.5. Differential thermal analysis and thermogravimetry

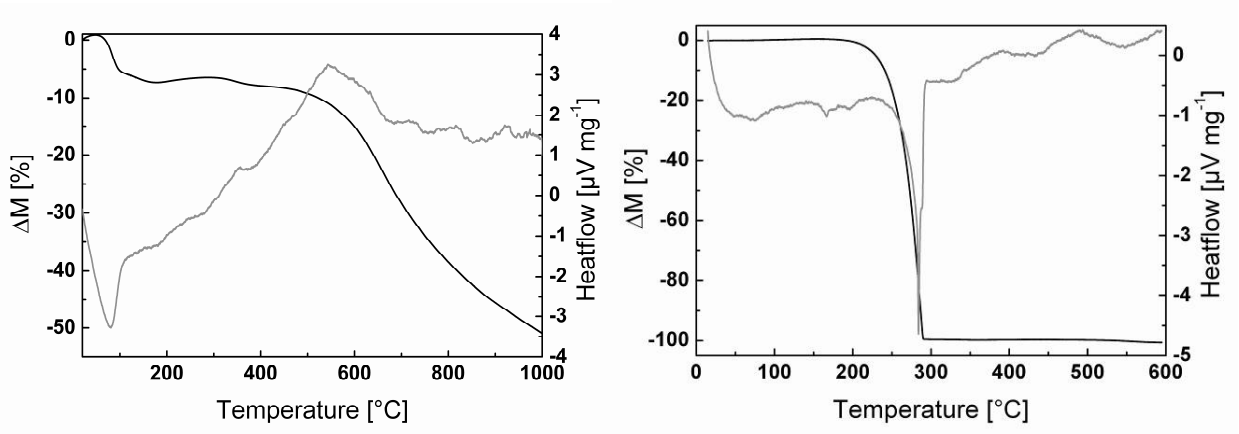


Figure S4. TG (black) and DTA (gray) curves of *bipy*-CTF-400 (left) and 5,5'-dicyano-2,2'-bipyridine (right).

2.6. Infrared spectroscopy

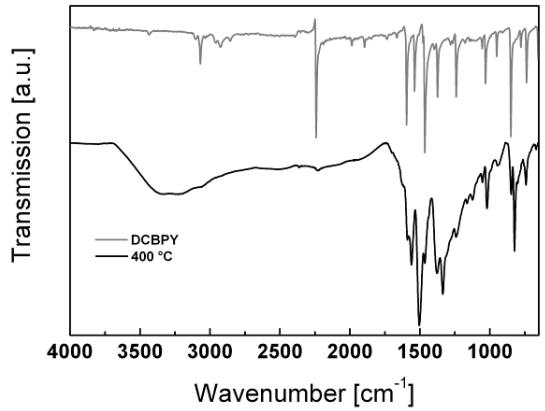


Figure S5. IR spectra of *bipy*-CTF-400 and DCBPY.

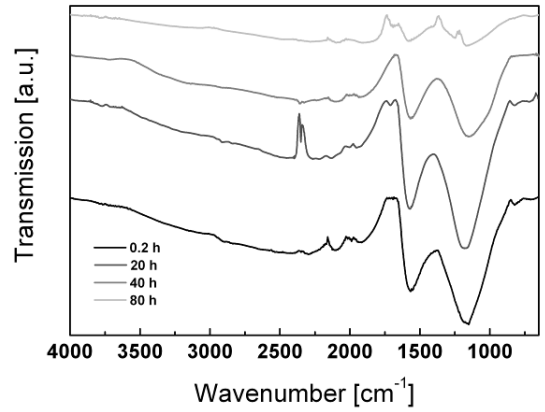
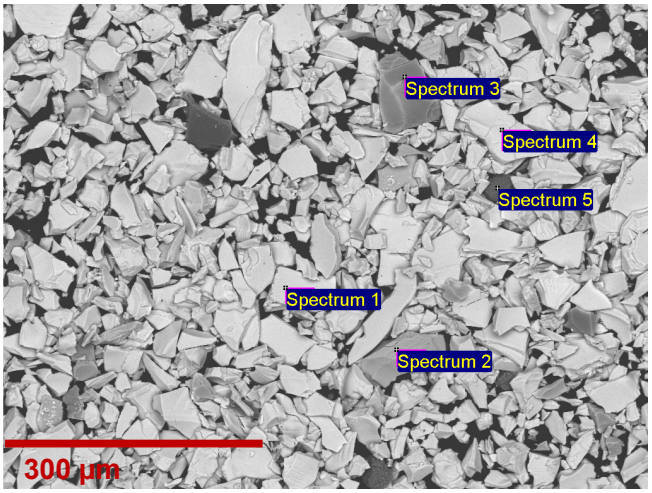


Figure S6. IR spectra of *bipy*-CTFs obtained with different temperature programs (black 0.2 h, dark gray 20 h, gray 40 h and light gray 80 h.

2.7. Scanning electron microscopy



Spectrum	In stats.	O	Si	Cl	Pt
Spectrum 1	Yes			67.11	32.89
Spectrum 2	No			71.35	28.65
Spectrum 3	No			75.38	24.62
Spectrum 4	Yes			67.04	32.96
Spectrum 5	No	60.88	39.12		
Max.		0.00	0.00	67.11	32.96
Min.		0.00	0.00	67.04	32.89

All results in atomic%

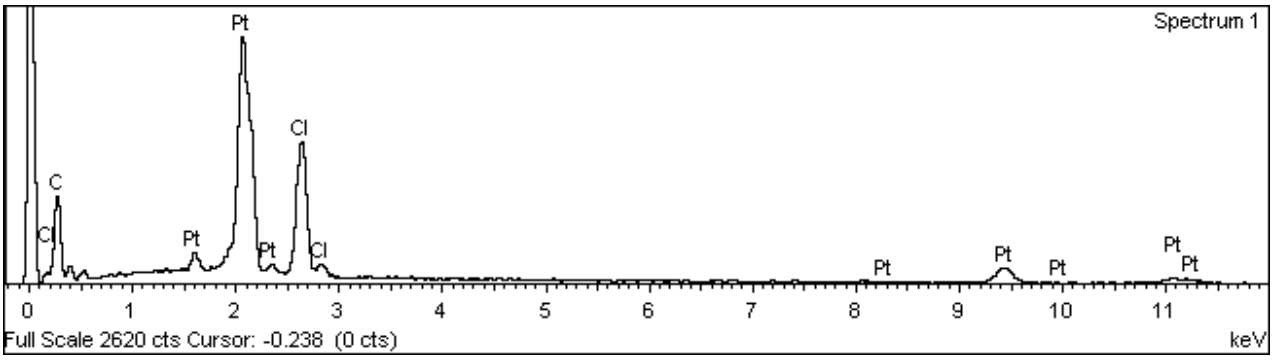


Figure S7. SEM image of a Pt loaded sample with corresponding EDX values and the EDX spectra of the spot Spectrum 1.

2.8. Elemental analysis

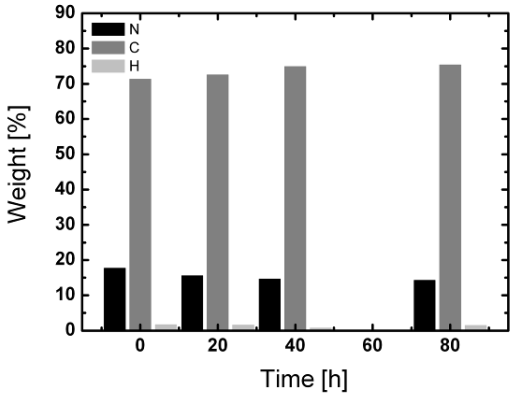


Figure S8. Variation of carbon, hydrogen and nitrogen contents as a function of the synthesis time at 600 °C.