Electronic Supplementary Information for RSC Advances

Zinc-Doped Covalent organic Frameworks as High-Efficiency Chemiresistors for Acetylene Gas Detection

Prerana Loomba [a,b], Sujith Benarzee Nallamalla [a], Suresh Koppula [c], Naresh Kumar Katari [d]*, Manabolu Surya Surendra Babu [a]**

[a] *Department of Chemistry, GITAM School of Science, GITAM Deemed to be University, Hyderabad, Telangana-502329, India*

[b] *Department of Chemistry, Bhavan's Vivekananda College of Science, Humanities & Commerce, Sainikpuri, Hyderabad, Telangana, India*

[c] *ACUBIOSYS Private Limited, Telangana State Industrial Infrastructure Corporation Limited—Industrial Area Local Authority (TSIIC-IALA), Hyderabad, India*

[d] *School of Chemistry & Physics, College of Agriculture, Engineering & Science, Westville Campus, University of KwaZulu-Natal, P Bag X 54001, Durban 4000, South Africa.*

***Correspondence:**smanabol@gitam.edu; KatariN@ukzn.ac.za; dr.n.k.katari@gmail.com

Table of Contents

Section S-1 : ^{13}C NMR

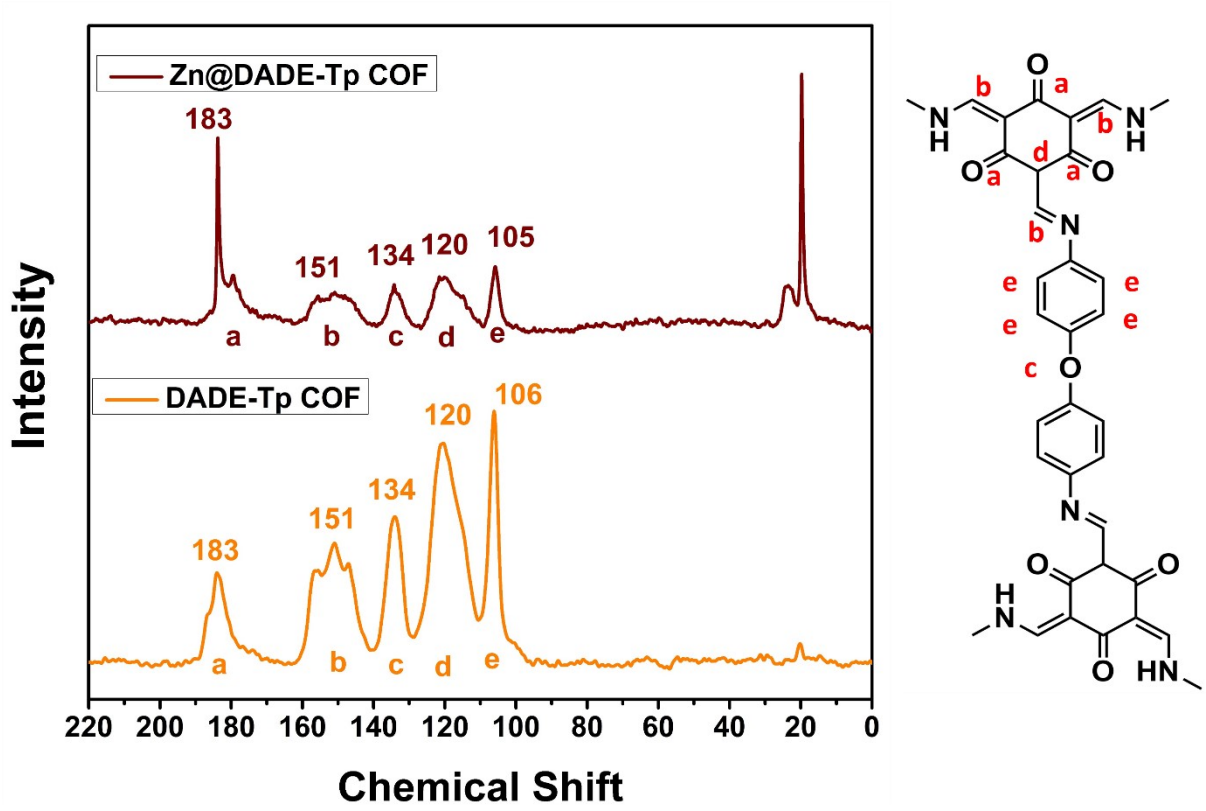

Figure S1: ^{13}C CP-MAS solid-state NMR spectra for DADE-Tp COF and Zn@DADE-Tp COF

Section S-2 : EDX and elemental mapping

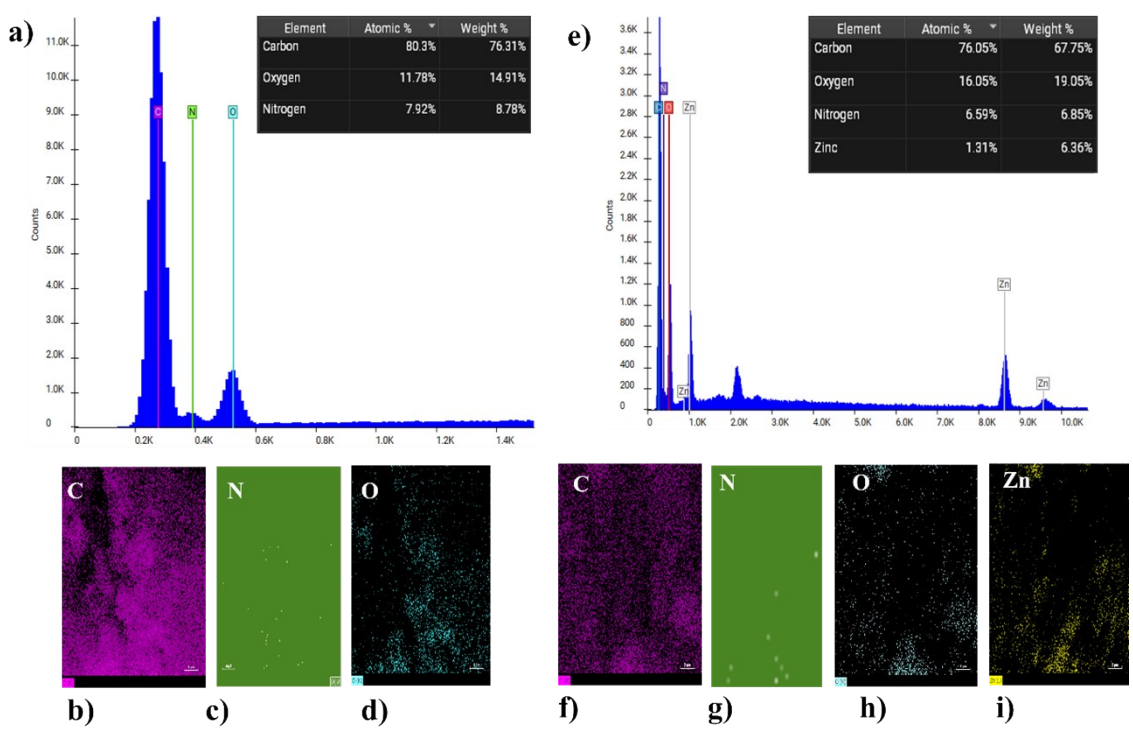

Figure S2: a) to d) EDX and elemental mapping of DADE-Tp COF, e) to i) EDX and elemental mapping of Zn@DADE-Tp COF.

Section S-3 : Thermogravimetric analysis (TGA)

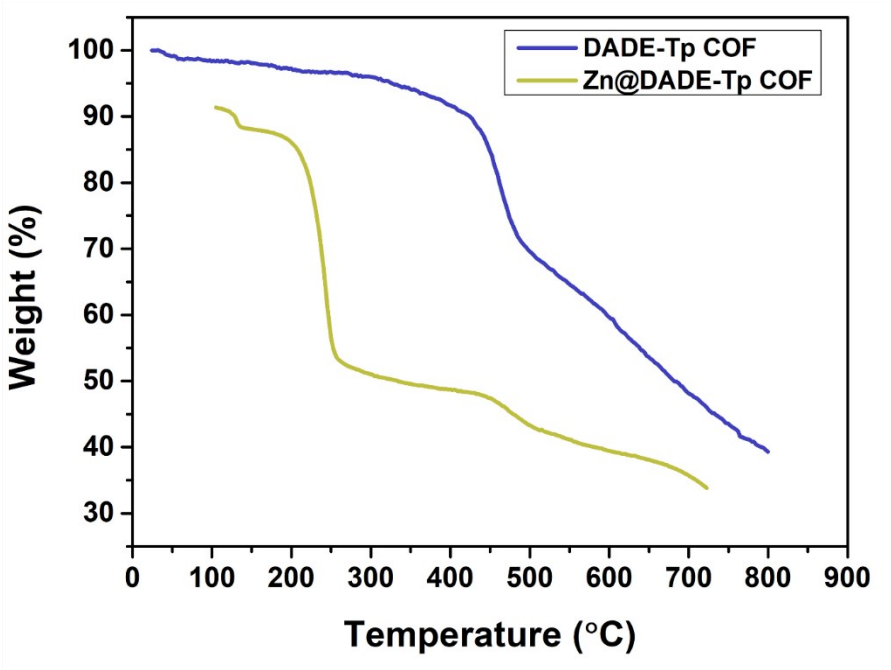

Figure S3: Thermogravimetric analysis (TGA) comparison of DADE-Tp COF and Zn@DADE-Tp COF

Section S-4 : Atomic Force Microscopy (AFM)

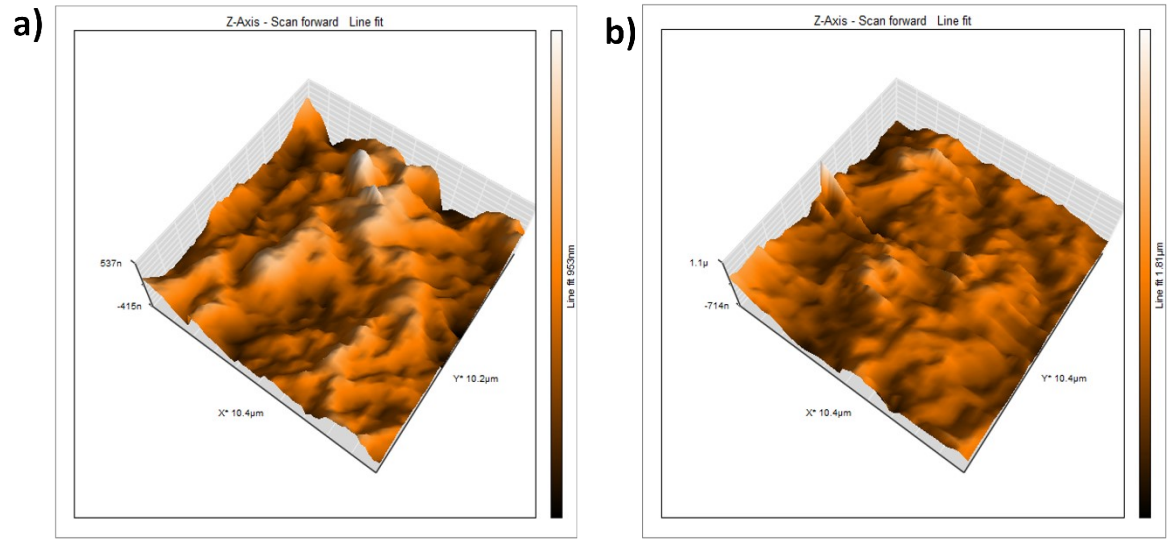

Figure S4: a) AFM images for DADE-Tp COF, b) AFM images for Zn@DADE-Tp COF

Section S-5: X-ray photoelectron spectroscopy (XPS)

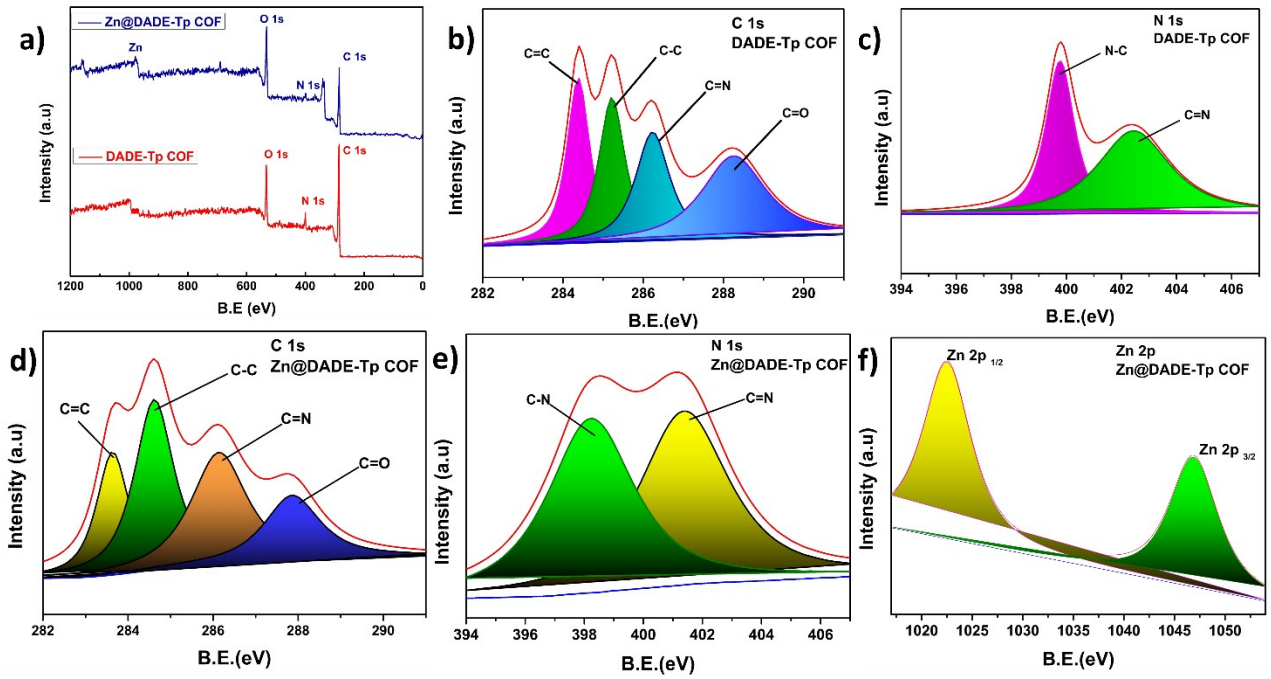

Figure S5: a) Survey scan for DADE-Tp COF and Zn@DADE-Tp COF b) to f) XPS Split for DADE-Tp COF and Zn@DADE-Tp COF. b) C1s split for DADE-Tp COF, b) N1s split for DADE-Tp COF, d) C1s split for Zn@DADE-Tp COF, e) N1s split for Zn@DADE-Tp COF, f) Zn 2p split for Zn@DADE-Tp COF

Section S-6 : Brunauer–Emmett–Teller (BET) analysis

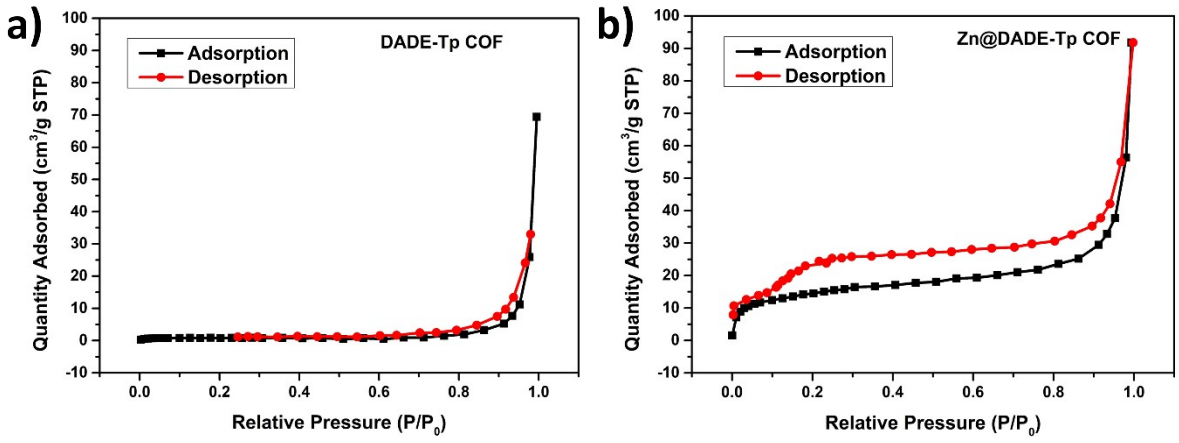

Figure S6: N2 - adsorption and desorption studies on a) DADE-Tp COF, b) Zn@DADE-Tp COF.

Section S-7 : Gas sensing set up

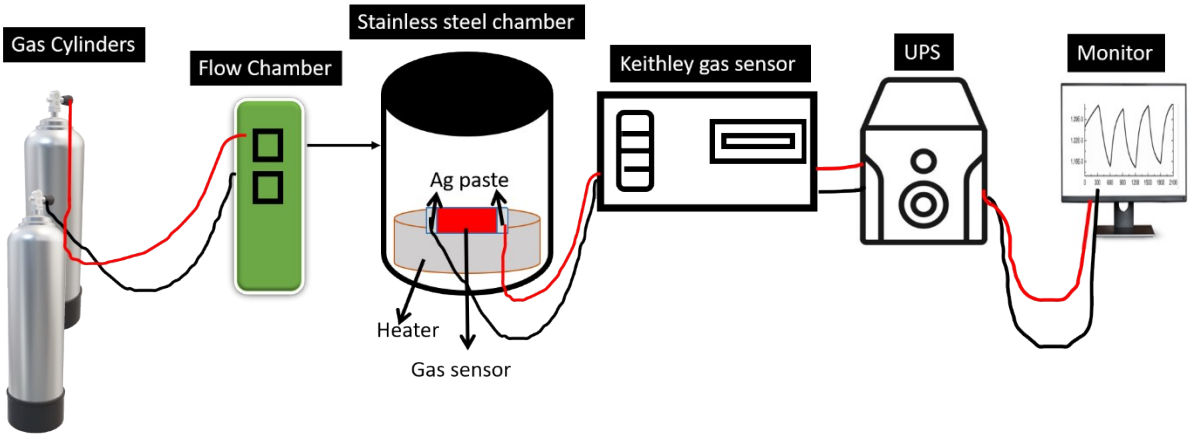

Figure S7: Schematic illustration of the acetylene gas sensing instrument setup

Section S-8: Geometrical optimized structure

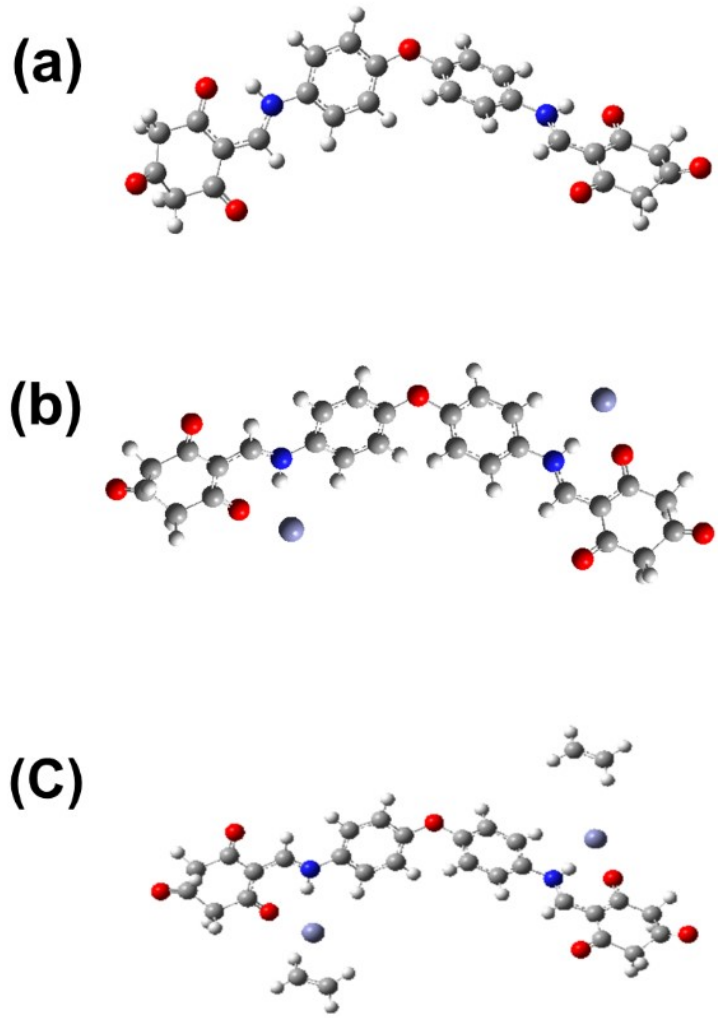

Figure S8. Geometrical optimized structure of (a) DADE-Tp COF, (b) Zn@DADE-Tp COF , and (c) Zn@DADE-Tp COF-Acetylene

Section S-8 : Tables

Table S1. Fractional atomic coordinates for DADE-Tp COF, Zn@DADE-Tp COF and Zn@DADE-Tp COF with Acetylene.

DADE-Tp COF			
C	19.7657	-16.5359	0
C	19.7657	-17.8659	0
C	20.9175	-18.5309	0
C	22.0694	-17.8659	0
C	22.0694	-16.5359	0
C	20.9175	-15.8709	0
N	20.9175	-19.8609	0
O	20.9175	-14.5409	0
C	20.9175	-13.2109	0
C	22.0694	-12.5459	0
C	22.0694	-11.2159	0
C	20.9175	-10.5509	0
C	19.7657	-11.2159	0
C	19.7657	-12.5459	0
N	20.9175	-9.2209	0
C	22.0693	-8.5559	0
C	19.7657	-20.5259	0
C	19.7657	-21.8559	0
C	18.6139	-22.5209	0
C	20.9175	-22.5209	0
O	17.4621	-21.8559	0
C	18.6138	-23.8509	0
C	20.9175	-23.8509	0
C	19.7657	-24.5159	0
O	22.0693	-21.856	0
O	19.7656	-25.8459	0
C	22.0693	-7.2259	0
C	23.2211	-6.5609	0
C	20.9175	-6.5609	0
C	20.9175	-5.2309	0
C	22.0694	-4.5659	0
C	23.2212	-5.231	0
O	22.0694	-3.2359	0
O	24.373	-7.226	0
O	19.7657	-7.2259	0
H	18.83905	-16.0009	0
H	18.83905	-18.4009	0

H	22.99604	-18.4009	0
H	22.99604	-16.0009	0
H	21.35051	-20.1109	0.866025
H	22.99604	-13.0809	0
H	22.99604	-10.6809	0
H	18.83905	-10.6809	0
H	18.83905	-13.0809	0
H	20.48449	-8.9709	0.866025
H	22.99595	-9.0909	0
H	18.83905	-19.9909	0
H	18.15047	-24.1184	-0.92665
H	18.15047	-24.1184	0.926647
H	21.38082	-24.1184	0.926647
H	21.38082	-24.1184	-0.92665
H	20.45418	-4.96339	0.926647
H	20.45418	-4.96339	-0.92665
H	23.68454	-4.96353	0.926647
H	23.68454	-4.96353	-0.92665

Zn@DADE-Tp COF			
C	-1.36848	-0.75655	1.012278
C	-2.6257	-0.15324	0.95189
C	-3.67686	-0.80064	0.285813
C	-3.4654	-2.05342	-0.31313
C	-2.21072	-2.65263	-0.25824
C	-1.16455	-1.99999	0.4008
N	-4.98621	-0.25708	0.177299
O	0.050212	-2.69779	0.489044
C	1.292753	-2.05023	0.424436
C	2.329461	-2.63604	1.15949
C	3.616689	-2.10499	1.097065
C	3.862007	-0.9782	0.296763
C	2.818049	-0.39913	-0.44148
C	1.532817	-0.93361	-0.38508
N	5.139665	-0.36605	0.177065
C	6.273214	-0.71654	0.779145
C	-5.42366	0.914455	0.632342
C	-6.73149	1.406993	0.504291
C	-6.97368	2.731147	1.090618
C	-7.7677	0.655521	-0.14158
O	-6.07508	3.371895	1.682127
C	-8.36156	3.34594	0.945103
C	-9.16912	1.227331	-0.24758
C	-9.46806	2.336587	0.741304
O	-7.55245	-0.49953	-0.6503
O	-10.5579	2.417111	1.322996
C	7.513524	-0.07747	0.624662

C	8.624398	-0.6473	1.397306
C	7.686371	1.047036	-0.24712
C	9.048848	1.69967	-0.38653
C	10.20845	0.824071	0.045295
C	9.989627	0.026513	1.310434
O	11.27086	0.787669	-0.58908
O	8.477591	-1.64838	2.134957
O	6.715405	1.53908	-0.92216
H	-0.55868	-0.26581	1.53836
H	-2.76872	0.806179	1.43482
H	-4.30031	-2.5352	-0.81785
H	-2.03014	-3.61834	-0.71375
H	-5.68028	-0.8344	-0.31073
H	2.1131	-3.50546	1.767916
H	4.406779	-2.5737	1.671517
H	3.039579	0.46835	-1.06027
H	0.735186	-0.49084	-0.96887
H	5.199644	0.444817	-0.44903
H	6.259533	-1.56848	1.451991
H	-4.72315	1.561302	1.151575
H	-8.334	4.009335	0.063888
H	-8.57211	3.973295	1.814074
H	-9.8992	0.42088	-0.13944
H	-9.28879	1.629668	-1.26771
H	9.048661	2.608851	0.238197
H	9.190287	2.027484	-1.41976
H	10.06943	0.714558	2.169293
H	10.77242	-0.72623	1.427496
Zn	4.767896	2.274047	-1.96397
Zn	-6.8585	-2.5366	-1.55179
C	4.309561	5.239131	0.32251
C	5.541916	4.776687	-7E-08
H	6.410075	5.353146	0.242685
H	5.646765	3.835106	-0.49732
H	4.17882	6.263705	0.601896
H	3.467294	4.579681	0.297763
C	-6.97118	-5.95535	0.535235
C	-5.73882	-6.41779	0.212724
H	-4.87067	-5.84134	0.455409
H	-5.63398	-7.35938	-0.2846
H	-7.10192	-4.93078	0.81462
H	-7.81345	-6.6148	0.510488

Zn@DADE-Tp COF-Acetylene

C	-1.36848	-0.75655	1.012278
C	-2.6257	-0.15324	0.95189

C	-3.67686	-0.80064	0.285813
C	-3.4654	-2.05342	-0.31313
C	-2.21072	-2.65263	-0.25824
C	-1.16455	-1.99999	0.4008
N	-4.98621	-0.25708	0.177299
O	0.050212	-2.69779	0.489044
C	1.292753	-2.05023	0.424436
C	2.329461	-2.63604	1.15949
C	3.616689	-2.10499	1.097065
C	3.862007	-0.9782	0.296763
C	2.818049	-0.39913	-0.44148
C	1.532817	-0.93361	-0.38508
N	5.139665	-0.36605	0.177065
C	6.273214	-0.71654	0.779145
C	-5.42366	0.914455	0.632342
C	-6.73149	1.406993	0.504291
C	-6.97368	2.731147	1.090618
C	-7.7677	0.655521	-0.14158
O	-6.07508	3.371895	1.682127
C	-8.36156	3.34594	0.945103
C	-9.16912	1.227331	-0.24758
C	-9.46806	2.336587	0.741304
O	-7.55245	-0.49953	-0.6503
O	-10.5579	2.417111	1.322996
C	7.513524	-0.07747	0.624662
C	8.624398	-0.6473	1.397306
C	7.686371	1.047036	-0.24712
C	9.048848	1.69967	-0.38653
C	10.20845	0.824071	0.045295
C	9.989627	0.026513	1.310434
O	11.27086	0.787669	-0.58908
O	8.477591	-1.64838	2.134957
O	6.715405	1.53908	-0.92216
H	-0.55868	-0.26581	1.53836
H	-2.76872	0.806179	1.43482
H	-4.30031	-2.5352	-0.81785
H	-2.03014	-3.61834	-0.71375
H	-5.68028	-0.8344	-0.31073
H	2.1131	-3.50546	1.767916
H	4.406779	-2.5737	1.671517
H	3.039579	0.46835	-1.06027
H	0.735186	-0.49084	-0.96887
H	5.199644	0.444817	-0.44903
H	6.259533	-1.56848	1.451991
H	-4.72315	1.561302	1.151575
H	-8.334	4.009335	0.063888
H	-8.57211	3.973295	1.814074
H	-9.8992	0.42088	-0.13944

H	-9.28879	1.629668	-1.26771
H	9.048661	2.608851	0.238197
H	9.190287	2.027484	-1.41976
H	10.06943	0.714558	2.169293
H	10.77242	-0.72623	1.427496
Zn	4.767896	2.274047	-1.96397
Zn	-6.8585	-2.5366	-1.55179
C	4.309561	5.239131	0.32251
C	5.541916	4.776687	-7E-08
H	6.410075	5.353146	0.242685
H	5.646765	3.835106	-0.49732
H	4.17882	6.263705	0.601896
H	3.467294	4.579681	0.297763
C	-6.97118	-5.95535	0.535235
C	-5.73882	-6.41779	0.212724
H	-4.87067	-5.84134	0.455409
H	-5.63398	-7.35938	-0.2846
H	-7.10192	-4.93078	0.81462
H	-7.81345	-6.6148	0.510488

Table S2. Geometrically optimized COFs energy values.

S. No	Sample Name	Optimized energy
1.	DADE-Tp COF	-1638.42 Hartree
2.	Zn@DADE-Tp COF	-5196.62 Hartree
3.	Zn@DADE-Tp - C_2H_2	-5353.77 Hartree

Table S3. HOMO energies (E_{HOMO}) LUMO energies (E_{LUMO}) and energy gap calculated for DADE-Tp COF, Zn@DADE-Tp COF, and Zn@DADE-Tp - C_2H_2.

S. No	Sample Name	E_{LUMO}	E_{HOMO}	Energy gap value (eV)
1	DADE-Tp COF	-2.43	-6.17	3.74
2	Zn@DADE-Tp COF	-2.70	-5.35	2.64
3	Zn@DADE-Tp - C_2H_2	-2.67	-5.27	2.59

Table S4 Selected π →π* donor-acceptor interactions in Zn@DADE-Tp COF With Acetylene from NBO analysis, showing stabilization energy (E(2)), energy gap(ΔE), and Fock matrix element (F(I,j)).*

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
π C 3 - C 4	π* C 1 - C 2	21.07	0.28	0.069
π C 3 - C 4	π* C 5 - C 6	20.12	0.28	0.067
π C 5 - C 6	π* C 1 - C 2	20.7	0.28	0.068
π C 5 - C 6	π* C 3 - C 4	21.36	0.28	0.069
π C 9 - C 14	π* C 12 - C 13	21.26	0.28	0.07
π C 10 - C 11	π* C 9 - C 14	20.27	0.27	0.068
π C 12 - C 13	π* C 10 - C 11	20.16	0.28	0.068

Table S5. Natural population analysis (NPA) data for Zn atoms in Zn@DADE-Tp COF.

Atom No	Natural charge	Natural Population			
		Core	Valence	Rydberg	Total
Zn 56	0.03908	17.99973	11.9571	0.00409	29.96092
Zn 57	0.0394	17.99974	11.95678	0.00408	29.9606

Table S6. Natural population analysis (NPA) data for Zn atoms in Zn@DADE-Tp COF after acetylene adsorption.

Atom No	Natural charge	Natural Population			
		Core	Valence	Rydberg	Total
Zn 56	0.04891	17.9997	11.94704	0.00435	29.95109
Zn 57	0.03795	17.99972	11.95723	0.00509	29.96205