

Electronic Supplementary Information

Vis-to-NIR electrochromism and bright-to-dark electrofluorochromism in a triazine and thiophene based three-dimensional covalent polymer

Sayan Halder,^{a,#} Neelam Gupta,^{c,#} Ravi Prakash Behere^c, Biplab Kumar Kuila^{c,*} and Chanchal Chakraborty^{a,b*}

^aDepartment of Chemistry, Birla Institute of Technology & Science (BITS) Pilani, Hyderabad Campus, Samirpet, Hyderabad, Telangana 500078, India

^bMaterials Center for Sustainable Energy & Environment (McSEE), Birla Institute of Technology and Science, Hyderabad Campus, Hyderabad 500078, India

^cDepartment of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, Uttar Pradesh, India

*Corresponding Author: Chanchal Chakraborty (chanchal@hyderabad.bits-pilani.ac.in)

ORCID ID: <https://orcid.org/0000-0002-4829-1367>

Biplab Kumar Kuila (bkkuila.chem@bhu.ac.in)

Sayan Halder, and Neelam Gupta contributed equally for the paper.

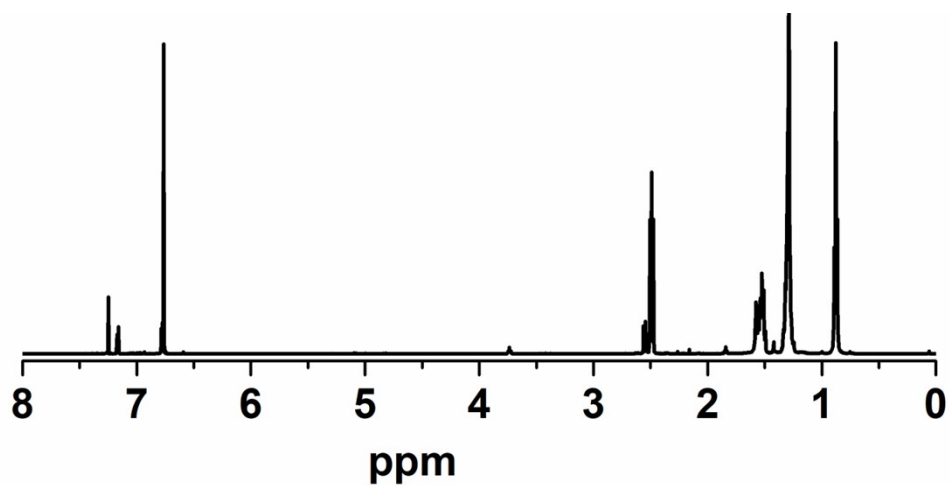


Fig. S1. ¹H NMR spectra of 2,5-dibromo-3-hexyl thiophene (7)

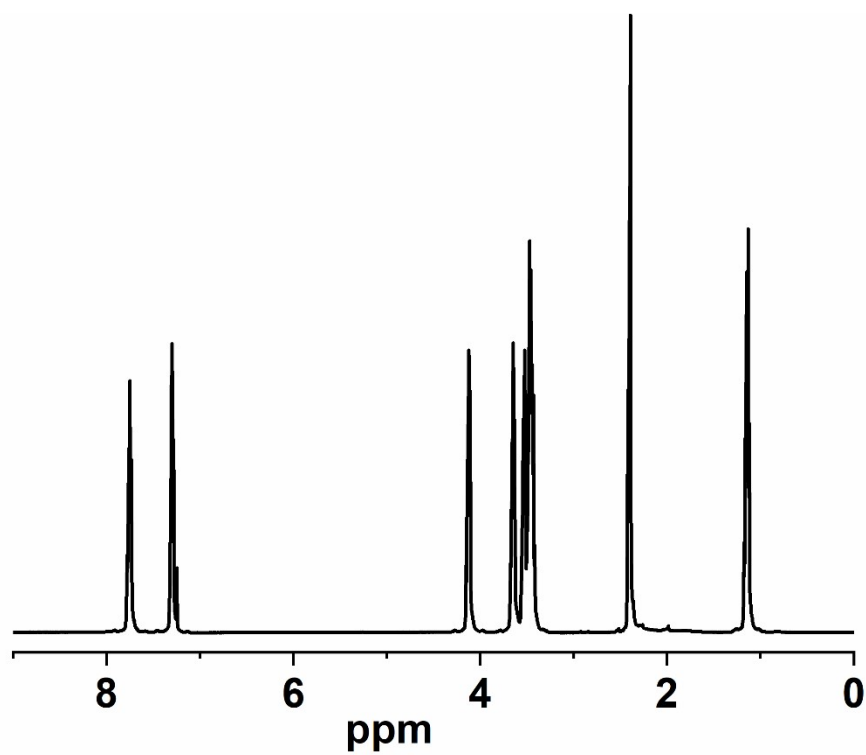


Fig. S2. ¹H NMR spectra of 2-(2-ethoxyethoxy)ethyl 4-methylbenzenesulfonate (2).

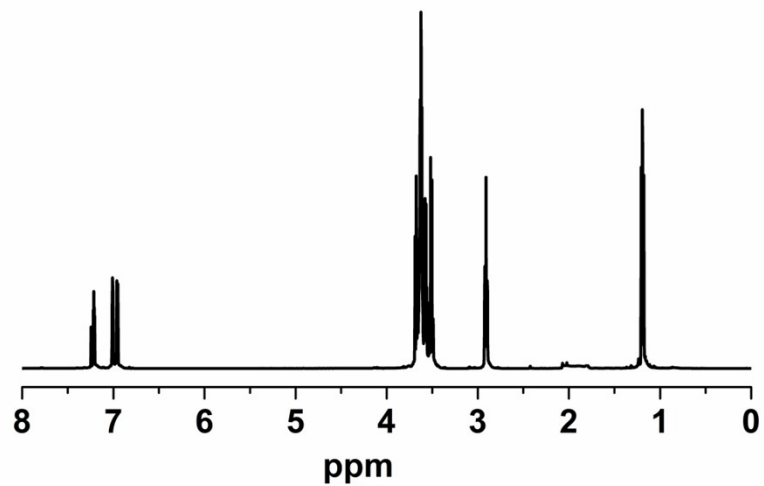


Fig. S3. ^1H NMR spectra of 3-(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)thiophene (4).

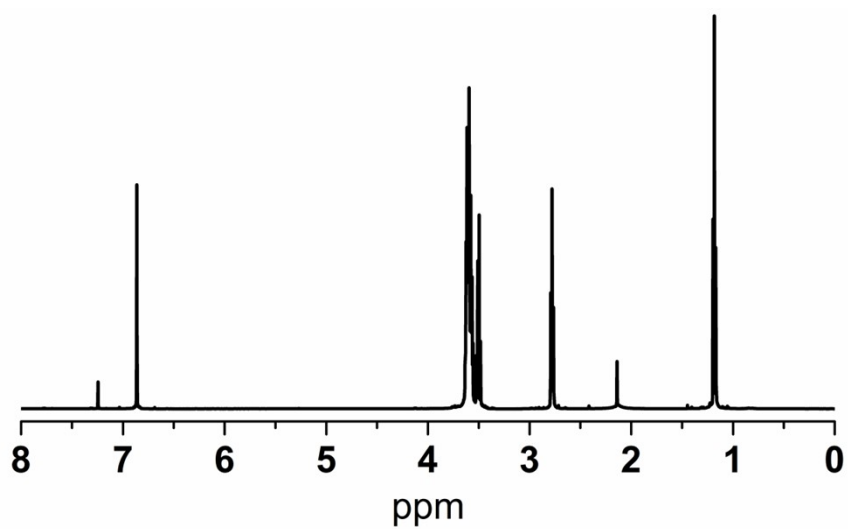


Fig. S4. ^1H NMR spectra of 2,5-dibromo-3-(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)thiophene (5).

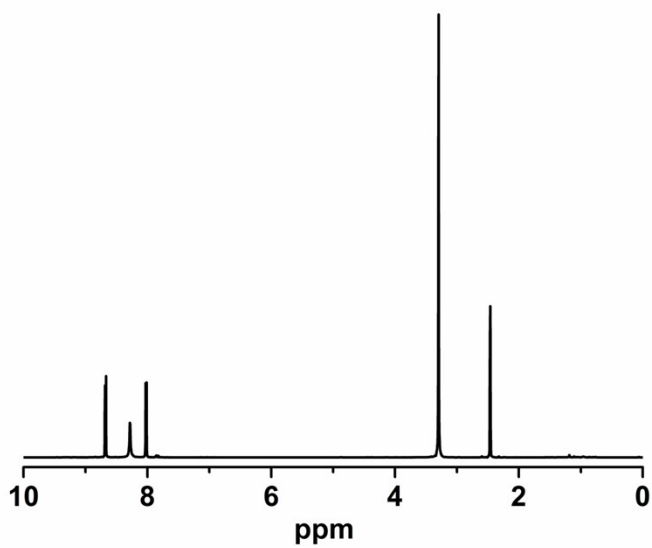


Fig. S5. ^1H NMR spectra of((1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))triboronic acid (9)

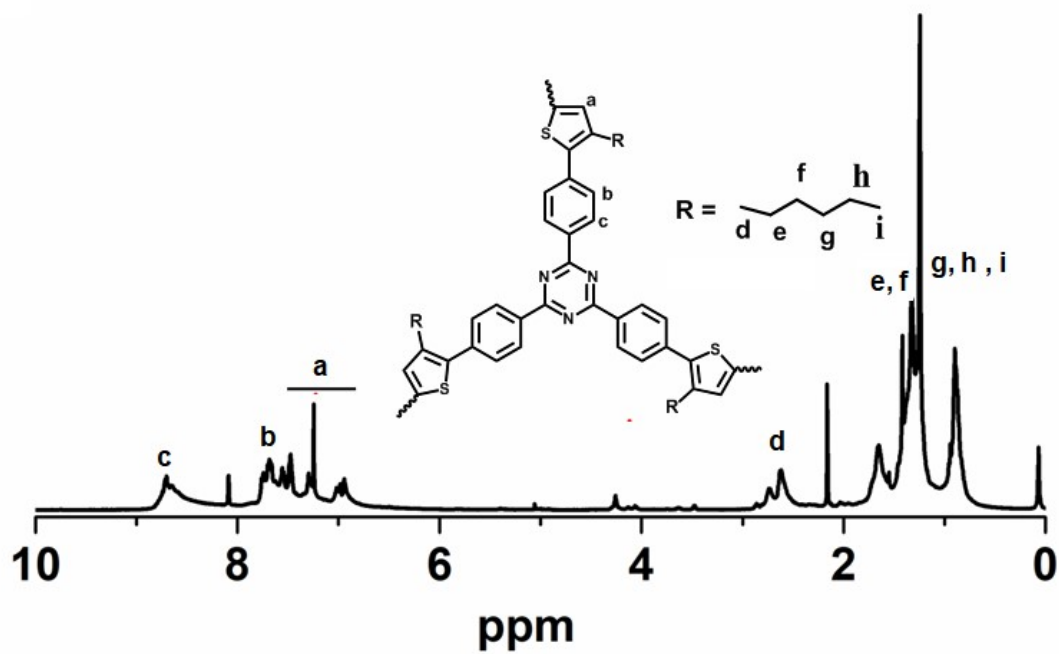


Fig. S6. ^1H NMR spectra of polymer CPF1 with peak assigned

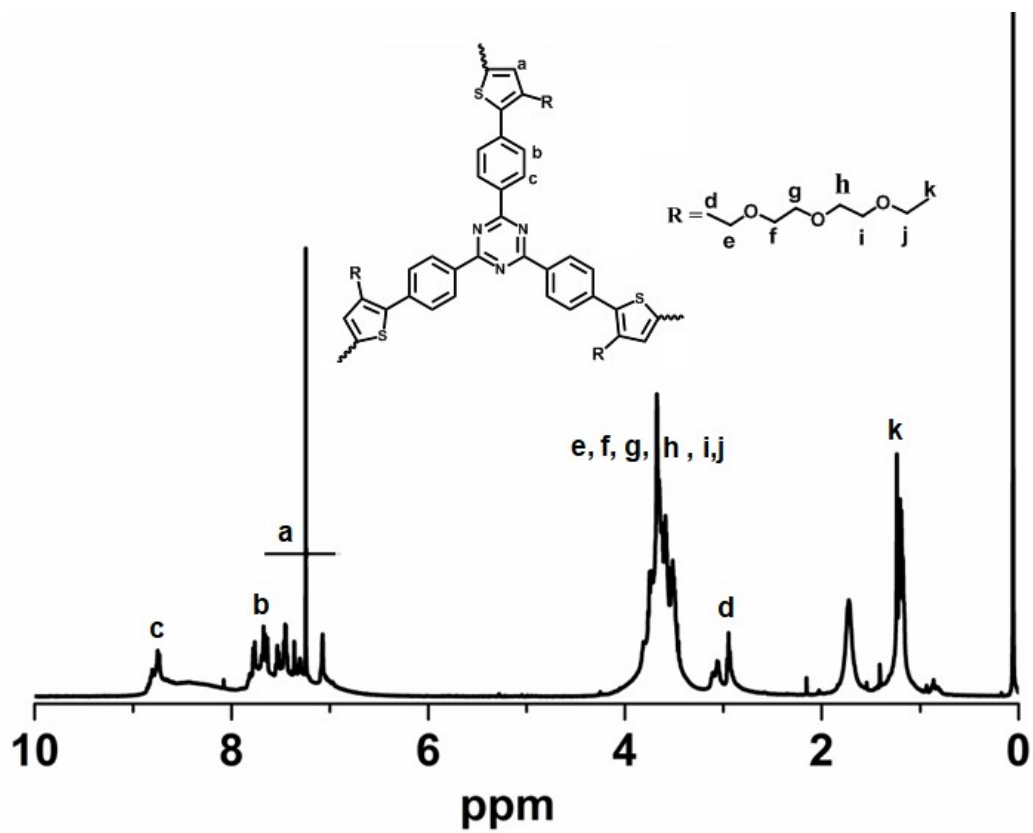


Fig. S7. ¹H NMR spectra of polymer CPF2 with peak assigned.

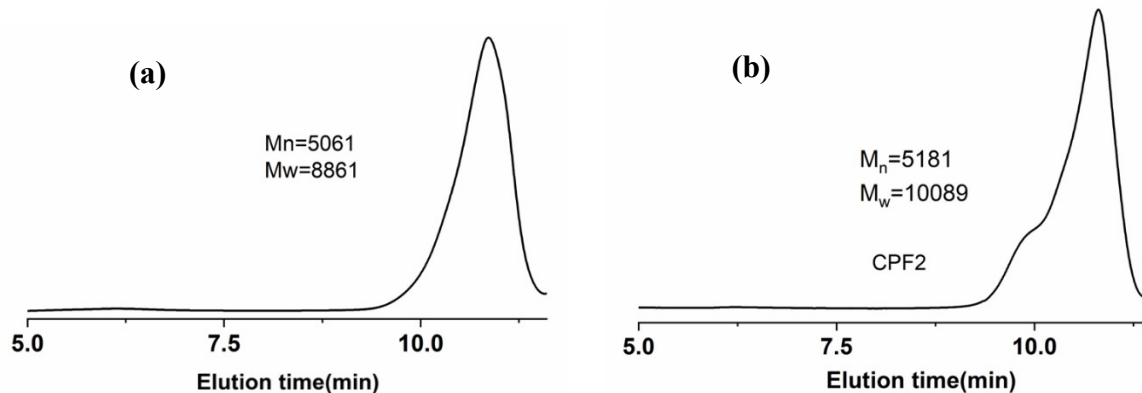


Fig. S8. GPC traces for the (a) CPF1 and (b) CPF2.

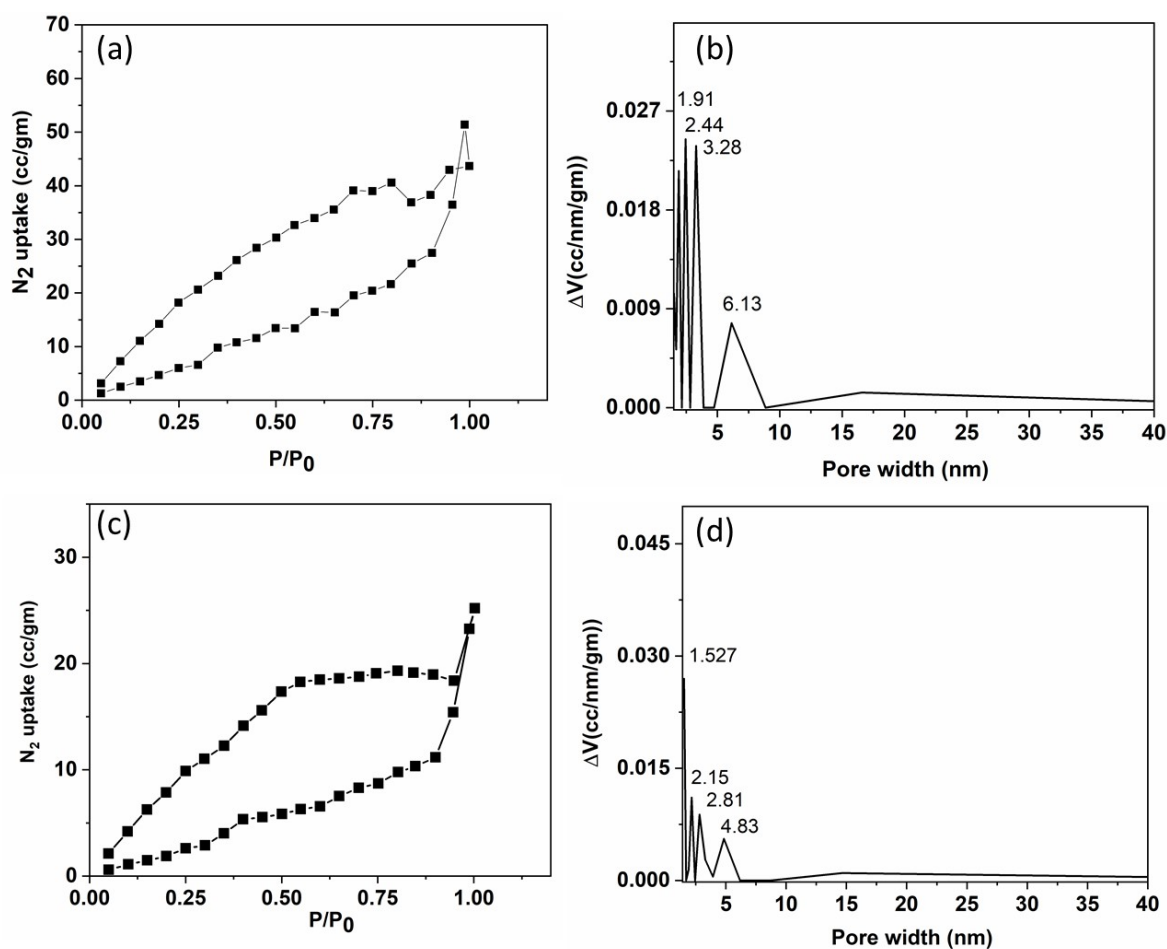


Fig. S9. (a) and (c) Nitrogen sorption isotherms of CPF1 and CPF2 measured at 77 K. (b) and (d) the pore size distribution of CPF1 and CPF2, respectively.

Summary of BET Data

CPF1

(i) BET summary

Surface Area = 34.68 m²/g

(ii) BJH adsorption summary

Surface Area = 29.49 m²/g

Pore Volume = 0.072 cc/g

Pore Radius Dv(r) = 24.467 Å

CPF2

(i) BET summary

Surface Area = 15.54 m²/g

(ii) BJH adsorption summary

Surface Area = 16.71 m²/g

Pore Volume = 0.042 cc/g

Pore Radius Dv(r) = 15.272 Å

Band gap study

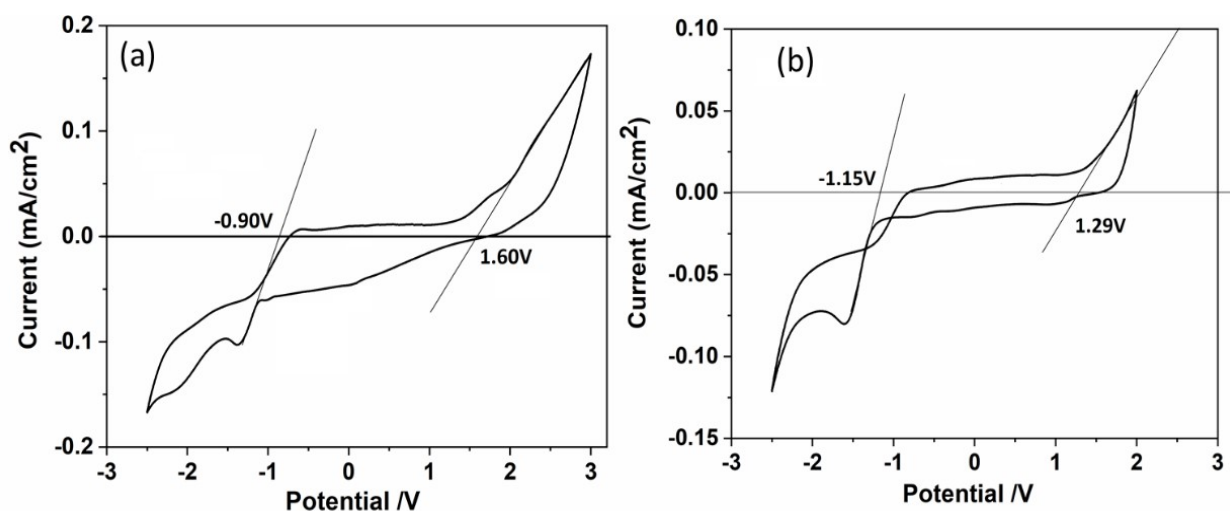


Fig. S10. Cyclic voltammetry of (a) CPF1 and (b) CPF 2 for the determination of HOMO, LUMO energy level and electronic band gap. CV was performed by taking the drop casted film of CPFs on glassy carbon electrode as working electrode, Pt as counter electrode and Ag/AgCl as reference electrode.

Band gap measured by following equation

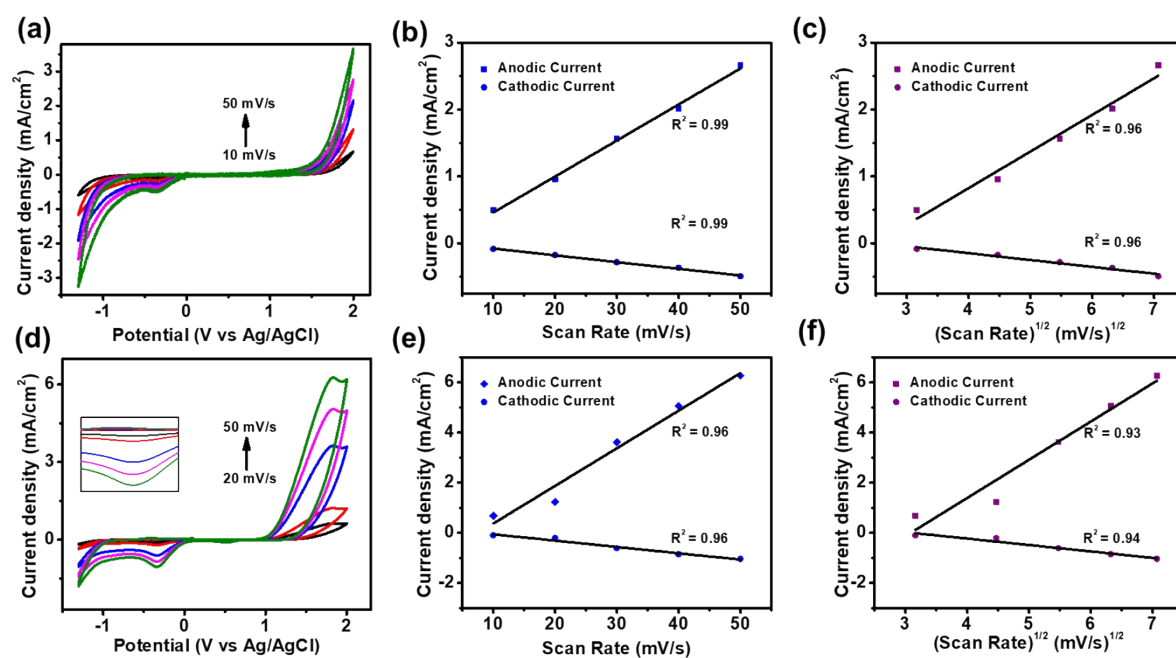
$$\text{HOMO} = -e (E_{\text{ox}} + 4.4) (\text{V})$$

$$\text{LUMO} = -e (E_{\text{red}} + 4.4) (\text{V})$$

$$E_{\text{g}} = e (E_{\text{ox}} - E_{\text{red}}) (\text{V})$$

Table S1. Summary of bandgap studies of the CPFs.

CPF	HOMO (eV)	LUMO (eV)	E_g (eV)
CPF1	-6.00	-3.50	2.50
CPF2	-5.69	-3.25	2.44



Electrochemical characterization

Fig. S11. (a) CV plot in different scan rates (0.1M TBAP/ ACN vs. Ag/AgCl, satd. KCl), (b) peak current density vs. scan rate plot, and (c) peak current vs. square root of scan rate for CPF1. (d) CV plot in different scan rates (0.1M TBAP/ ACN vs. Ag/AgCl, satd. KCl), (e) peak current density vs. scan rate plot, and (f) peak current vs. square root of scan rate for CPF2.

Table S2. EC and EFC colour changes of previously reported EC-EFC systems.

Derivatives	EC changes	EFC changes	Ref.
Tetraphenylethene containing triphenyl amine	colourless-to-black	Yellow to quenched	1
thiazolothiazole based viologen type molecule	Yellow to blue	Bright blueish to quenched	2,3
Fe-MSP with dye	Purple to pale red	Black to red	4
Thiophene based polymer	Yellow to NIR	Yellow to transparent	5
Arylamine-Fluorene based polymer	---	Bright to quenched	6
Dibenzofulvene derivative small molecules	Colorless to black	----	7
Terpyridine based gel	Transparent to black	Bright to quenched	8
Thiophene –triazine based COF	Yellow to brown	bluish-green to dark	This work

References:

- (1) T. Yu, Y. Han, H. Yao, Z. Chen and S. Guan, *Dyes Pigm.*, 2020, **181**, 108499-108506.
- (2) T. Adams, A. Brotherton, J. Molai, N. Parmar, J. Palmer, K. Sandor and M. Walter, *Adv. Funct. Mater.*, 2021, **31**, 2103408.
- (3) A. Woodward, J. Kolesar, S. Hall, N. Saleh, D. Jones and M. Walter, *J. Am. Chem. Soc.*, 2017, **139**, 8467-8473.
- (4) T. Suzuki, T. Sato, J. Zhang, M. Kanao, M. Higuchi and H. Maki, *J. Mater. Chem. C*, 2016, **4**, 1594-1598.
- (5) J. Liu, M. Li, J. Wu, Y. Shi, J. Zheng and C. Xu, *Org. Electron.* 2017, **51**, 295-303.

- (6) G. A. Corrente, E. Fabiano, M. L. Deda, F. Manni, G. Gigli, G. Chidichimo, A.-L. Capodilupo and A. Beneduci, *ACS Appl. Mater. Interfaces*, 2019, **11**, 12202-12208.
- (7) G. A. Corrente, E. Fabiano, F. Manni, G. Chidichimo, G. Gigli, A. Beneduci and A.-L. Capodilupo, *Chem. Mater.*, 2018, **30**, 5610-5620.
- (8) S. Halder, S. Roy, M. Dixit and C. Chakraborty, *Chem. Commun.*, 2022, **58**, 8368-8371.