

Sensitive photoluminescent chemosensor for cyanide in water based on a zinc coordination polymer bearing ditert-butyl-bipyridine.

Luis D. Rosales-Vázquez,^a Josue Valdes-García,^a Iván J. Bazany-Rodríguez,^a Juan M. Germán-Acacio,^b Diego Martínez-Otero,^c Alfredo R. Vilchis-Néstor,^c Raúl Morales-Luckie,^c Víctor Sánchez-Mendieta^{c*} and Alejandro Dorazco-González^{a*}

^a*Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México, 04510, CDMX., México.*

^b*Red de Apoyo a la Investigación, Universidad Nacional Autónoma de México-CIC, Instituto Nacional de Ciencias Médicas y Nutrición SZ, C. P.14000, Ciudad de México, México.*

^c*Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Ixtlahuaca Km. 14.5, Tlachaloya, Toluca, Estado de México, México.*

Corresponding authors: E-mail: adg@unam.mx (A. Dorazco-González); E-mail: vsanchezm@uaemex.mx (V. Sánchez-Mendieta)

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Table S1. Crystallographic data for the polymer, **1**Crystal data and structure refinement for Polymer (**1**)

Identification code	mo_050GOI16_0m	
Empirical formula	C ₂₀ H ₂₈ N ₂ O ₇ Zn	
Formula weight	473.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	a = 8.8493(6) Å b = 25.7425(15) Å c = 9.7652(6) Å	α = 90°. β = 106.8621(12)°. γ = 90°.
Volume	2128.9(2) Å ³	
Z	4	
Density (calculated)	1.478 Mg/m ³	
Absorption coefficient	1.198 mm ⁻¹	
F(000)	992	
Crystal size	0.454 x 0.168 x 0.112 mm ³	
Theta range for data collection	2.318 to 27.439°.	
Index ranges	-11<=h<=11, -28<=k<=33, -10<=l<=12	
Reflections collected	23490	
Independent reflections	4876 [R(int) = 0.0358]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4876 / 13 / 297	
Goodness-of-fit on F ²	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0716	
R indices (all data)	R1 = 0.0340, wR2 = 0.0741	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.487 and -0.319 e.Å ⁻³	

Table S2. Crystallographic data for the polymer, **2**Crystal data and structure refinement for Polymer **2**

Identification code	mo_117MLRA15_0m
Empirical formula	C20 H24 N2 O5 Zn
Formula weight	437.78
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	$a = 10.0221(5)$ Å $\alpha = 90^\circ$. $b = 20.7033(9)$ Å $\beta = 113.2768(10)^\circ$. $c = 10.1283(5)$ Å $\gamma = 90^\circ$.
Volume	1930.48(16) Å ³
Z	4
Density (calculated)	1.506 Mg/m ³
Absorption coefficient	1.307 mm ⁻¹
F(000)	912
Crystal size	0.388 x 0.234 x 0.052 mm ³
Theta range for data collection	1.967 to 26.371°.
Index ranges	-12<=h<=12, -25<=k<=25, -12<=l<=12
Reflections collected	38671
Independent reflections	3944 [R(int) = 0.0664]
Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3944 / 3 / 261
Goodness-of-fit on F ²	1.125
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0862
R indices (all data)	R1 = 0.0343, wR2 = 0.0873
Extinction coefficient	n/a
Largest diff. peak and hole	0.365 and -0.312 e.Å ⁻³

Table S3. Crystallographic data for the polymer, **3**Crystal data and structure refinement for Polymer (**3**)

Identification code	cu_096GOI16_0m
Empirical formula	C52 H86 N4 O17 Zn2
Formula weight	1169.98
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	Pn
Unit cell dimensions	$a = 9.2334(2)$ Å $\alpha = 90^\circ$. $b = 11.2034(3)$ Å $\beta = 95.9508(13)^\circ$. $c = 27.9409(7)$ Å $\gamma = 90^\circ$.
Volume	2874.78(12) Å ³
Z	2
Density (calculated)	1.352 Mg/m ³
Absorption coefficient	1.612 mm ⁻¹
F(000)	1244
Crystal size	0.362 x 0.069 x 0.044 mm ³
Theta range for data collection	3.180 to 68.242°.
Index ranges	-10≤h≤11, -13≤k≤13, -33≤l≤33
Reflections collected	24041
Independent reflections	8618 [R(int) = 0.0319]
Completeness to theta = 67.679°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8618 / 97 / 774
Goodness-of-fit on F ²	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0766
R indices (all data)	R1 = 0.0307, wR2 = 0.0773
Absolute structure parameter	0.49(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.448 and -0.269 e.Å ⁻³

Table S4 Hydrogen bonds for **1** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O(5)-H(5A)...O(6)	0.827(15)	1.934(16)	2.7535(19)	171(2)
O(5)-H(5B)...O(1)	0.834(15)	2.55(2)	2.9423(18)	110.3(17)
O(5)-H(5B)...O(2)	0.834(15)	1.799(15)	2.6193(18)	167(2)
O(6)-H(6A)...O(2)#3	0.839(15)	1.922(15)	2.7567(18)	173(2)
O(6)-H(6B)...O(7)#4	0.842(18)	1.997(17)	2.8328(19)	172(4)
O(6)-H(6C)...O(7)	0.830(18)	1.917(18)	2.741(2)	172(4)
O(7)-H(7A)...O(4)#1	0.850(15)	1.946(16)	2.7837(18)	169(2)
O(7)-H(7B)...O(6)	0.848(18)	1.91(2)	2.741(2)	168(4)
O(7)-H(7C)...O(6)#4	0.838(18)	2.007(19)	2.8328(19)	169(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1,y,z #3 -x+1,-y+1,-z #4 -x+2,-y+1,-z

Table S5 Hydrogen bonds for **2** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
C(5)-H(5)...O(4)#3	0.93	2.34	3.197(3)	153.5
O(5)-H(5A)...O(3)#4	0.828(17)	1.830(18)	2.657(3)	176(4)
O(5)-H(5B)...O(2)	0.843(17)	1.811(18)	2.618(3)	160(3)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1/2,z-1/2 #2 x+1,-y+1/2,z+1/2 #3 -x+1,y+1/2,-z+3/2
#4 x-1,y,z

Table S6. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(12)	0.84(2)	1.94(3)	2.732(4)	156(4)
O(5)-H(5B)...O(4)#1	0.83(2)	1.84(3)	2.645(4)	162(5)
O(10)-H(10A)...O(11)	0.83(2)	1.85(2)	2.676(4)	171(5)
O(10)-H(10B)...O(8)#2	0.83(2)	1.85(2)	2.673(4)	168(5)
O(11)-H(11A)...O(4)	0.88(2)	1.92(2)	2.765(4)	162(4)
O(11)-H(11B)...O(13)	0.85(2)	1.97(3)	2.751(5)	151(5)
O(12)-H(12D)...O(13)	0.84(2)	1.93(3)	2.709(5)	153(5)
O(12)-H(12E)...O(8)	0.85(2)	1.88(3)	2.706(4)	165(6)
O(13)-H(13D)...O(16)	0.87(2)	1.90(2)	2.737(5)	162(5)
O(13)-H(13E)...O(14)	0.87(2)	1.85(2)	2.713(5)	171(5)
O(14)-H(14D)...O(15)	0.92(2)	1.90(3)	2.818(5)	171(5)
O(14)-H(14E)...O(6)	0.88(2)	1.90(3)	2.763(4)	168(4)
O(15)-H(15A)...O(8)#2	0.90(2)	2.05(3)	2.939(5)	167(5)
O(15)-H(15B)...O(17)	0.89(2)	2.00(3)	2.844(4)	156(5)
O(16)-H(16D)...O(2)	0.88(2)	1.87(3)	2.748(4)	175(5)
O(16)-H(16E)...O(17)#1	0.88(2)	2.08(3)	2.905(5)	156(4)
O(17)-H(17D)...O(12)#2	0.89(2)	2.04(3)	2.901(5)	161(5)
O(17)-H(17E)...O(4)	0.86(2)	2.06(3)	2.909(5)	170(6)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 x+1,y,z

Table S7. Selected bond distances and bond angles for **1**

Bond	Distance (Å)	Bonds	Angles (°)
Zn(1)-O(1)	2.041(1)	O(1)-Zn(1)-N(2)	171.22(5)
Zn(1)-O(5)	2.079(1)	O(5)-Zn(1)-O(3)	163.52(5)
Zn(1)-N(1)	2.109(1)	N(1)-Zn(1)-O(4)	145.48(5)
Zn(1)-O(4)	2.142(1)	O(5)-Zn(1)-N(1)	108.24(6)
Zn(1)-N(2)	2.163(1)	O(5)-Zn(1)-O(4)	104.16(5)
Zn(1)-O(3)	2.256(1)	O(1)-Zn(1)-O(4)	96.80(5)
		O(4)-Zn(1)-N(2)	91.22(5)
		N(2)-Zn(1)-O(3)	87.12(5)
		N(1)-Zn(1)-O(3)	87.07(5)
		N(1)-Zn(1)-N(2)	77.15(6)
		O(4)-Zn(1)-O(3)	59.65(5)

Table S8. Selected bond distances and bond angles for **2**

Bond	Distance (Å)	Bonds	Angles (°)
Zn(1)-O(1)	1.988(2)	O(5)-Zn(1)-N(2)	169.49(9)
Zn(1)-O(3)	2.042(2)	O(4)-Zn(1)-O(1)	155.26(7)
Zn(1)-O(5)	2.050(2)	O(3)-Zn(1)-N(1)	136.61(8)
Zn(1)-N(1)	2.102(2)	O(1)-Zn(1)-N(1)	121.20(8)
Zn(1)-N(2)	2.172(2)	O(1)-Zn(1)-O(3)	99.86(8)
Zn(1)-O(4)	2.557(2)	O(5)-Zn(1)-N(1)	97.69(9)
		O(3)-Zn(1)-O(5)	95.36(10)
		O(3)-Zn(1)-N(2)	94.83(8)
		O(1)-Zn(1)-N(2)	85.48(8)
		N(1)-Zn(1)-N(2)	76.49(8)
		O(4)-Zn(1)-O(3)	55.40(7)

Table S9. Selected bond distances and bond angles for **3**

Bond	Distance (Å)	Bonds	Angles (°)
Zn(1)-O(1)	2.031(3)	O(3)-Zn(1)-N(2)	165.29(11)
Zn(1)-O(5)	2.057(3)	O(1)-Zn(1)-O(5)	151.33(12)
Zn(1)-O(3)	2.070(3)	N(1)-Zn(1)-O(2)	148.82(10)
Zn(1)-N(1)	2.111(3)	O(5)-Zn(1)-N(1)	113.32(11)
Zn(1)-N(2)	2.151(3)	O(3)-Zn(1)-O(2)	103.59(10)
Zn(1)-O(2)	2.488(3)	O(1)-Zn(1)-O(3)	95.32(11)
		O(1)-Zn(1)-N(2)	93.80(12)
		N(2)-Zn(1)-O(2)	91.05(11)
		O(5)-Zn(1)-N(2)	88.42(12)
		N(1)-Zn(1)-N(2)	76.28(12)
		O(1)-Zn(1)-O(2)	57.06(11)

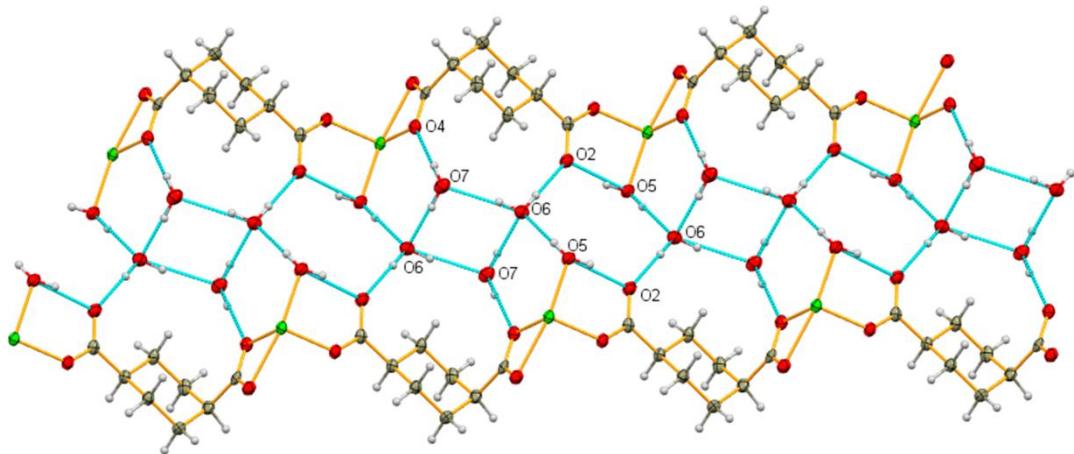


Fig. S1. 1D hydrogen-bonding supramolecular array of **1**; hydrogens are omitted for clarity.

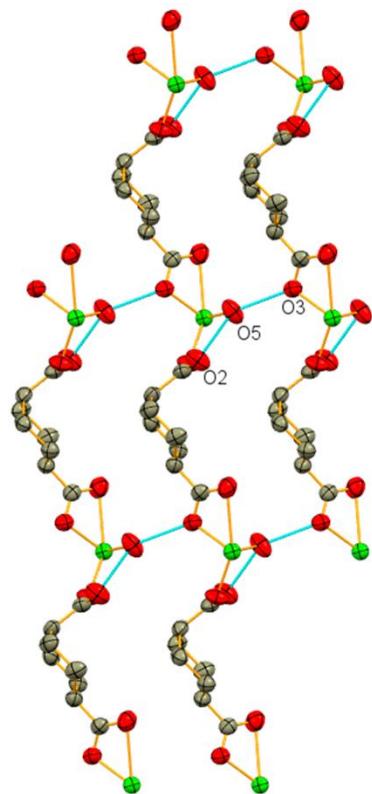


Fig. S2. 2D hydrogen-bonding supramolecular packing of **2**; 5dmb ligand is omitted for clarity.

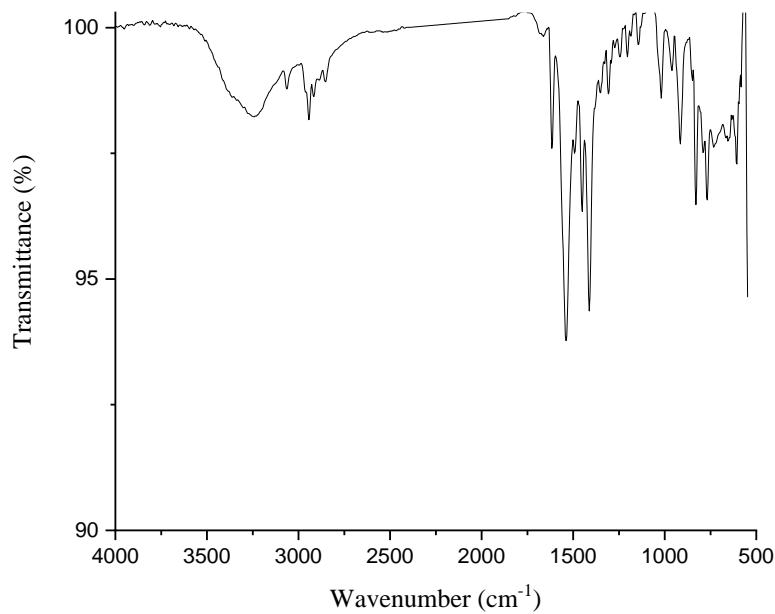


Fig. S3. IR-ATR of polymer, **1**

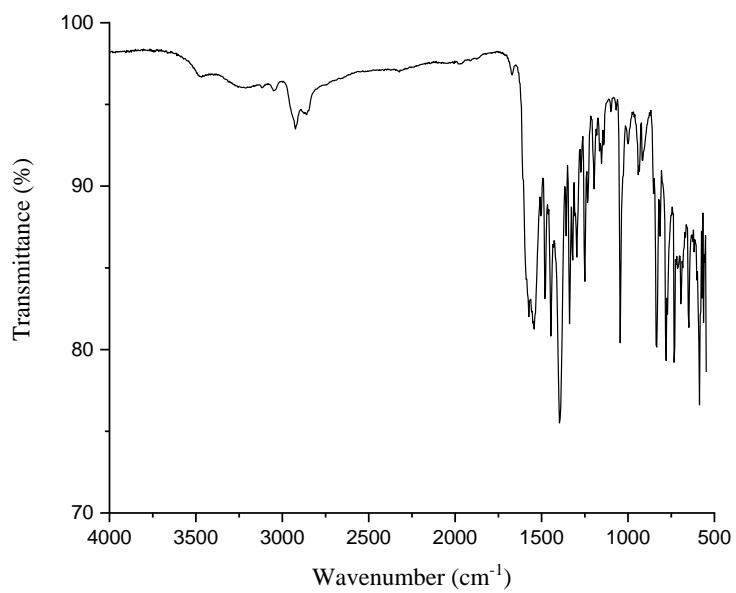


Fig. S4. IR-ATR of polymer, **2**

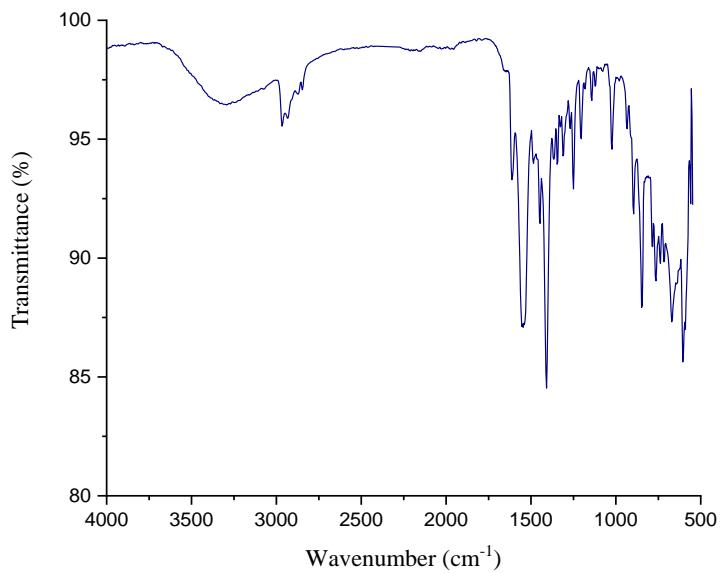


Fig. S5. IR-ATR of polymer, **3**

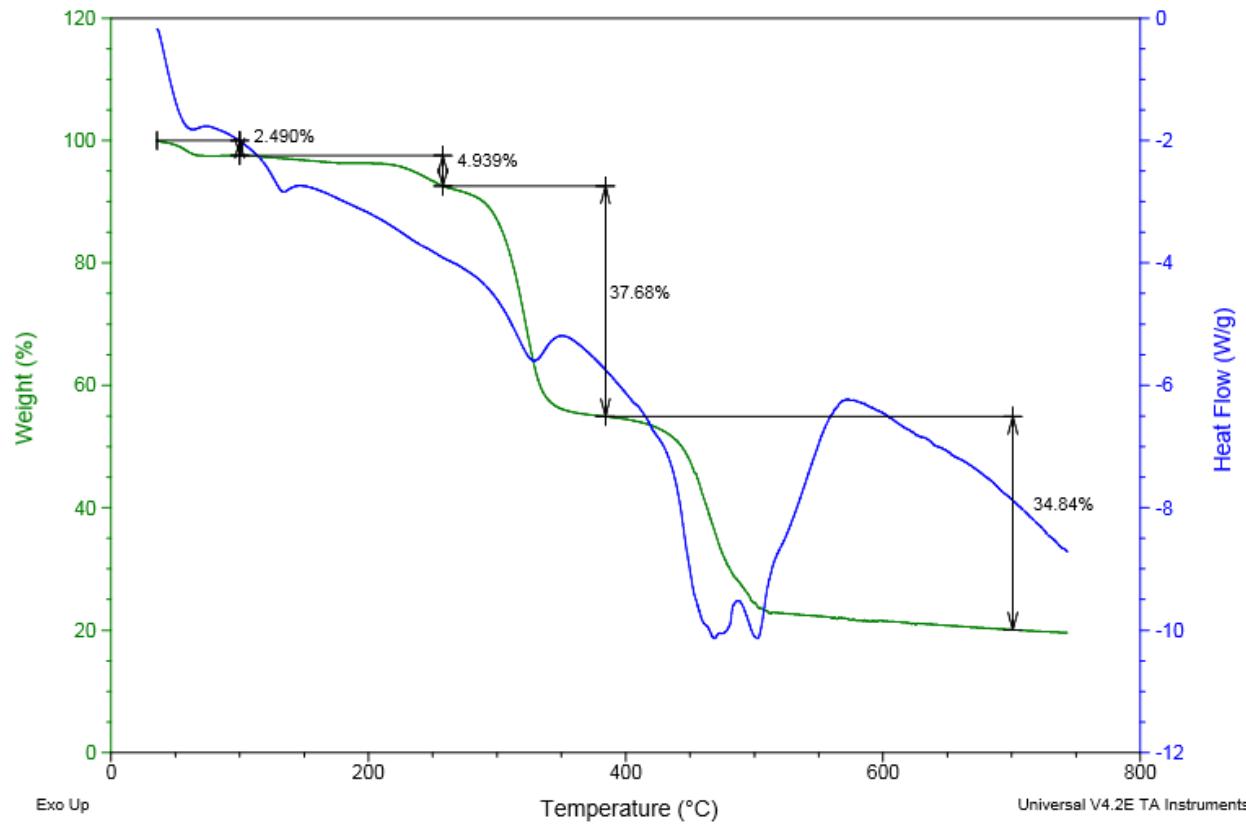


Fig. S6. TGA plots for polymer, **1**

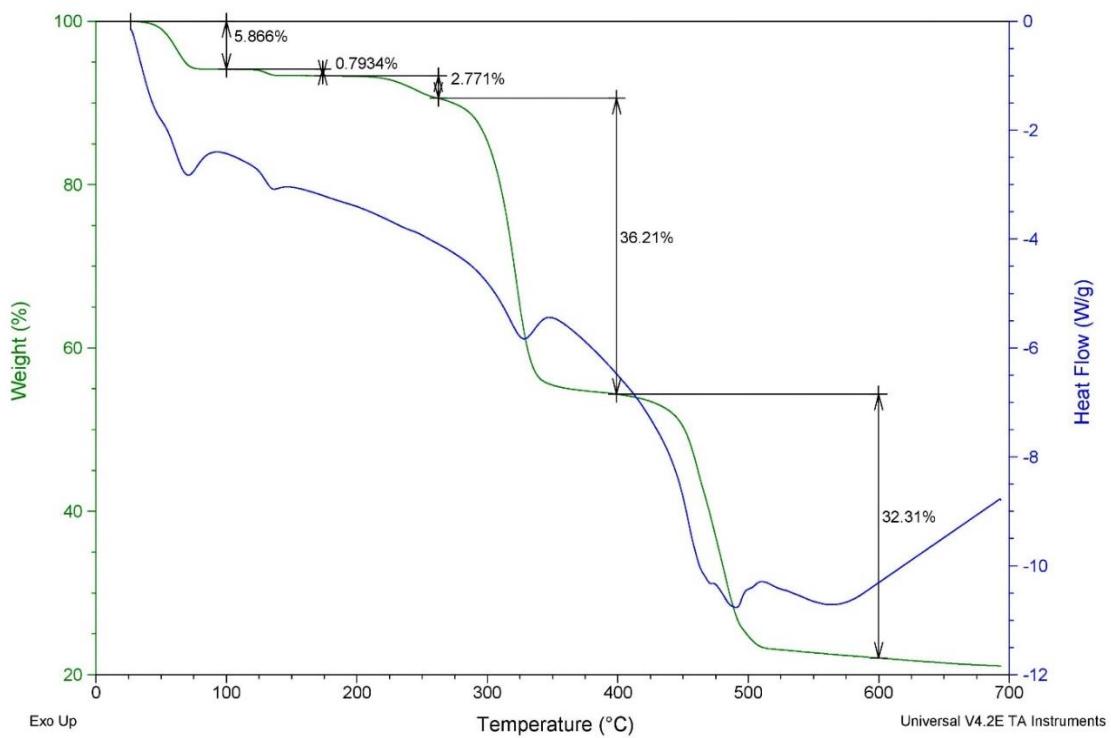


Fig. S7. TGA plots for polymer, 2

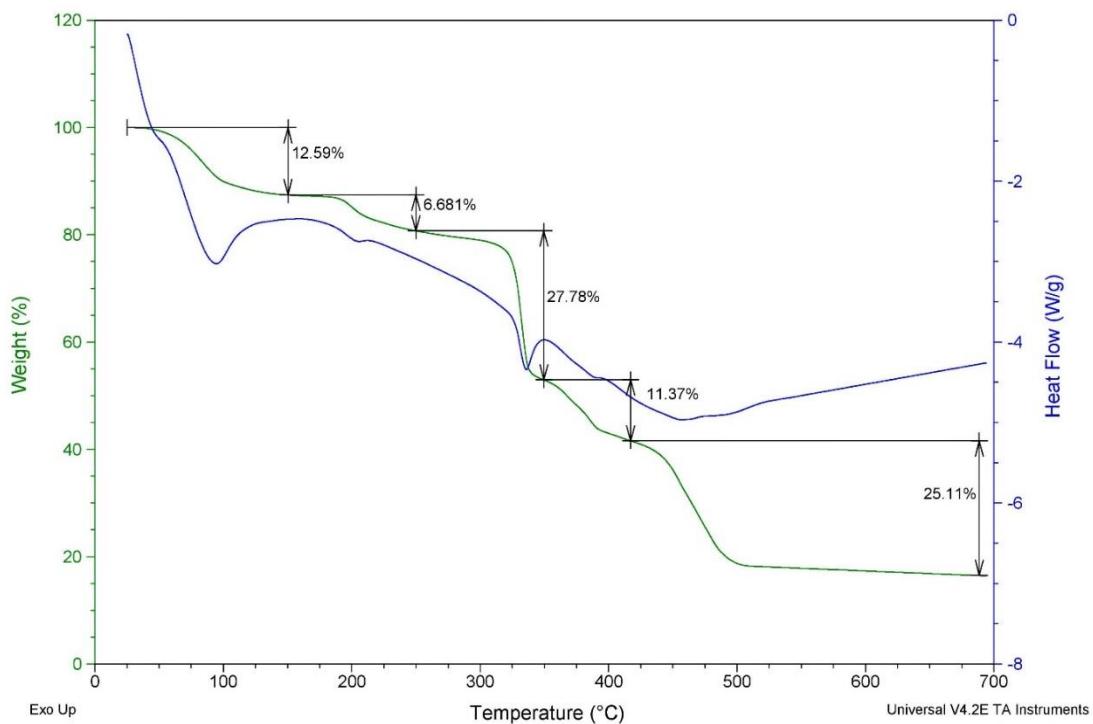


Fig. S8. TGA plots for polymer, 3

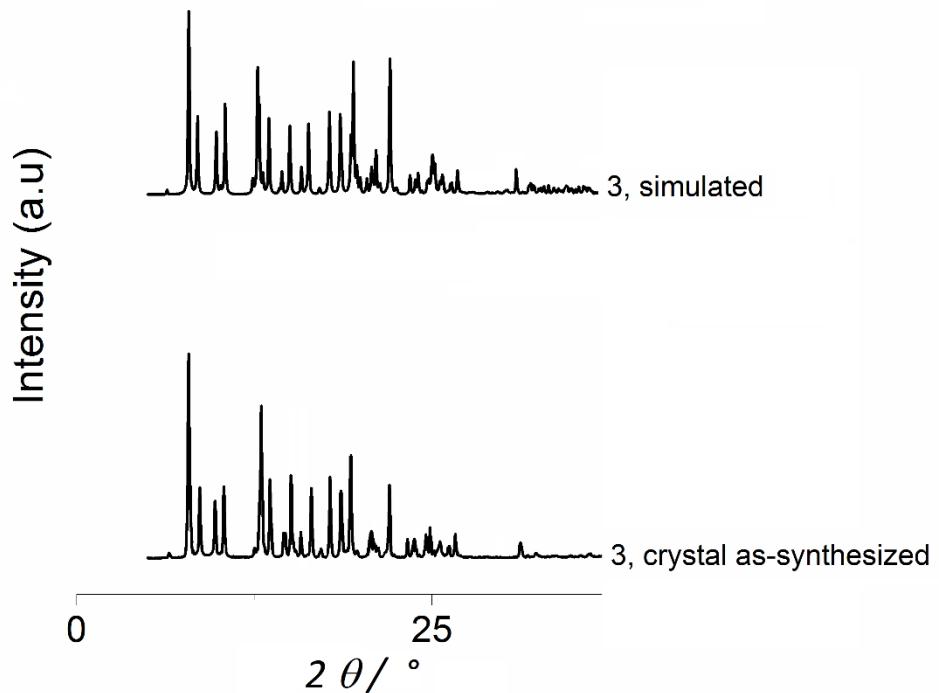


Fig. S9. PXRD pattern (bottom) and simulated patterns (top) for **3**.

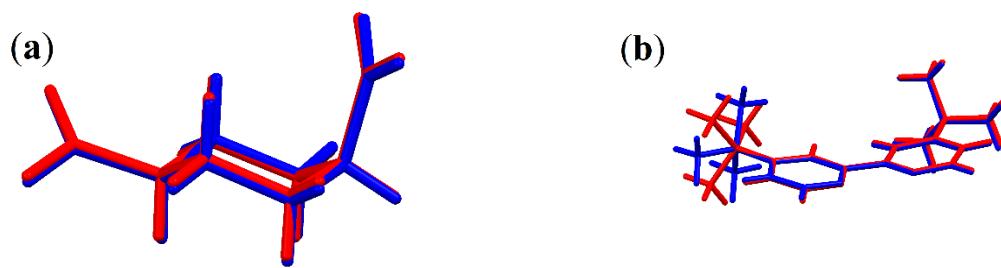


Fig. S10. Superimposed molecules 1,4-chdc and 4,4'-dtbb using the program Mercury. (a) According with the numbering of SCXRD colored in blue is the six-membered ring (C21, C22, C23, C24, C25, C26) and colored in red is the ring (C45, C46, C47, C48, C49, C50). (b) According with the numbering of SCXRD colored in blue are the atoms of 4,4'-dtbb molecule (C27, C28, C29, C30, C31, C32, C33, C34, C35, C36) and colored in red are the atoms (C1, C2, C3, C4, C5, C6, C7, C8, C9, C10).

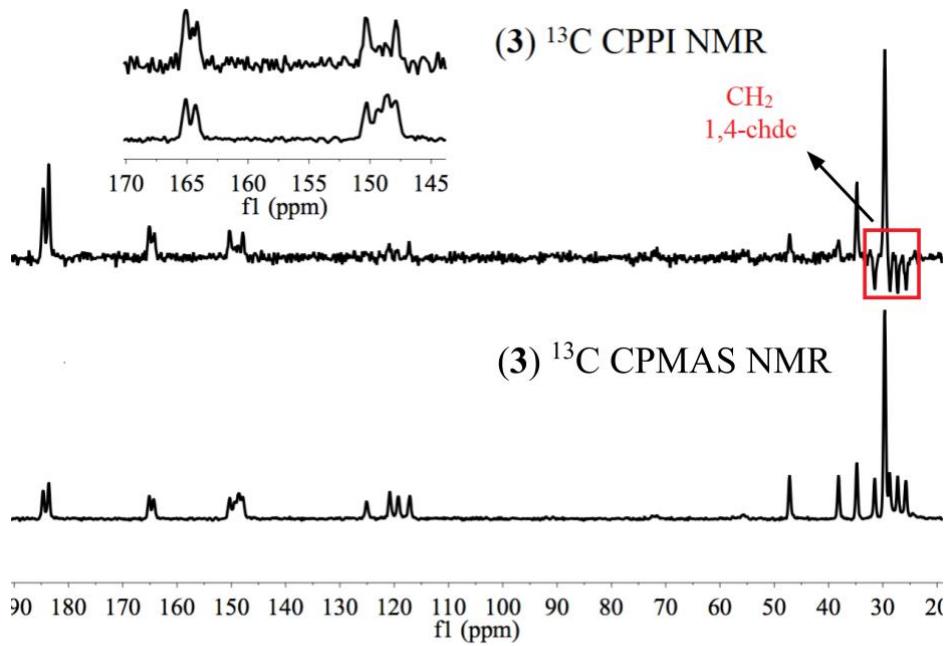


Fig. S11. ¹³C CPPI and CPMAS NMR spectra (spinning rate at 7kHz) of **3**. In the case of CPPI experiment 30 μ s of a polarization inversion period was used.

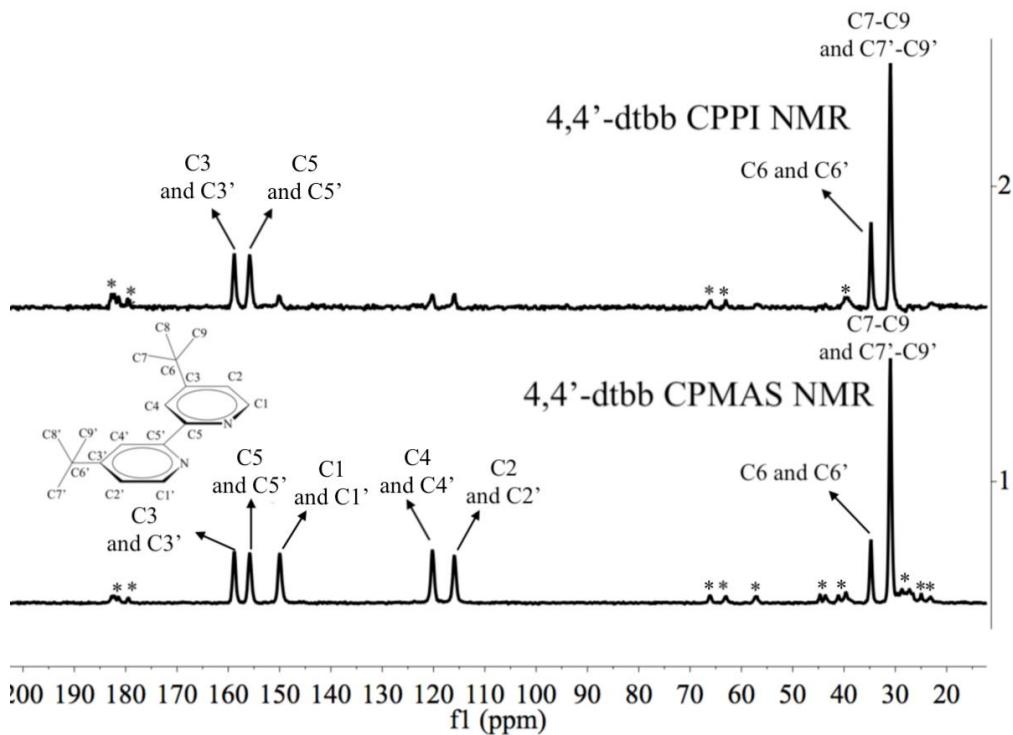


Fig. S12. ¹³C CPPI and CPMAS NMR (spinning rate at 7kHz) spectra of 4,4'-dtbb. In the case of CPPI experiment 30 μ s of a polarization inversion period was used.

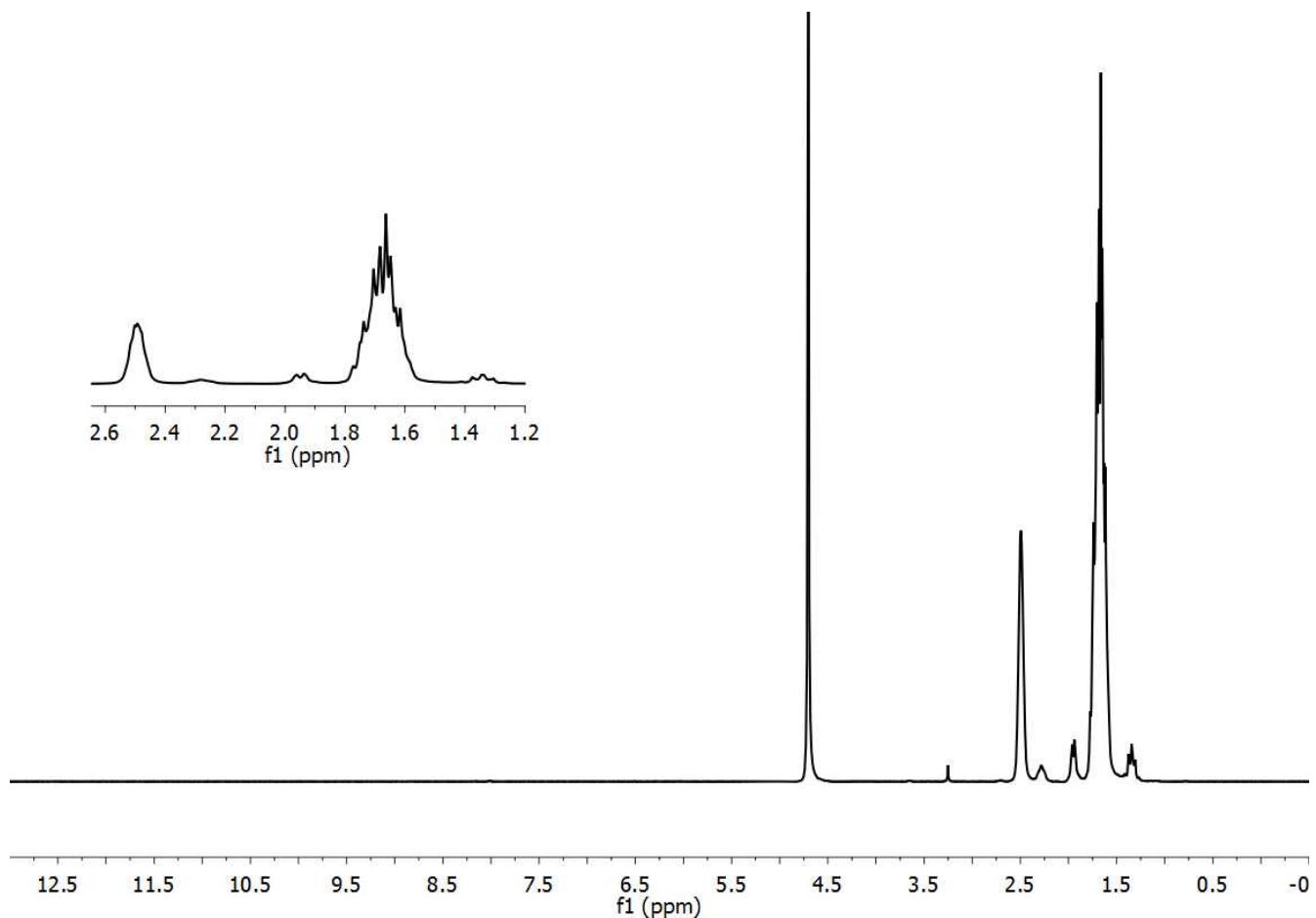


Figure S13. ¹H NMR spectrum of sodium salt of 1,4-cyclohexanedicarboxylato in D_2O

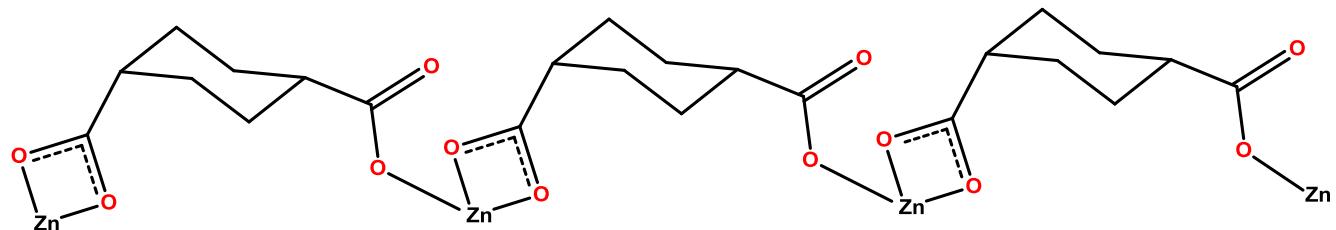


Fig. S14. Connectivity $RCOO-Zn$ for the polymers **1-2**.

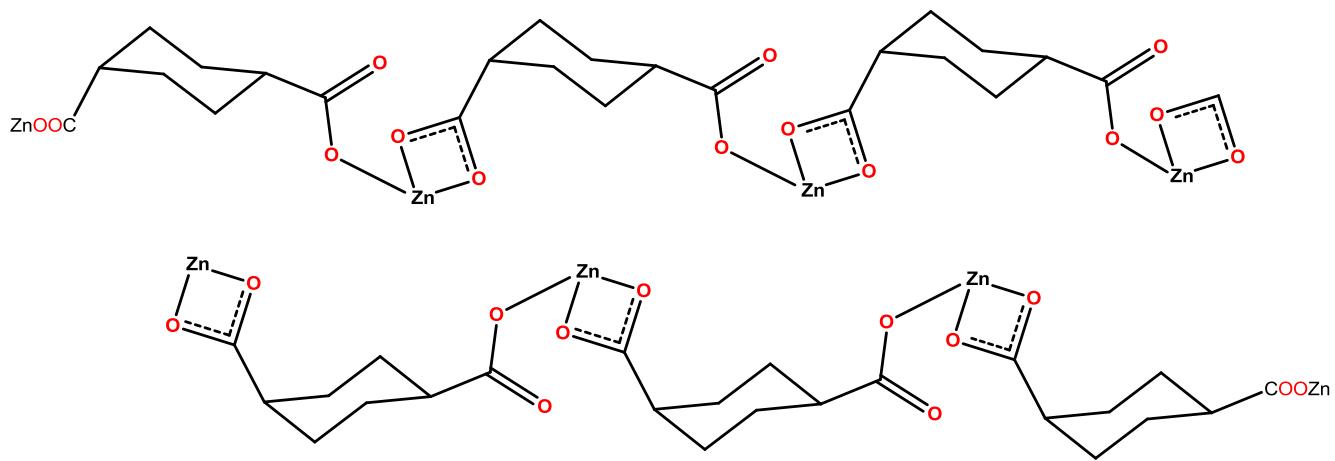


Fig. S15. Connectivity RCOO-Zn for the polymer **3**.

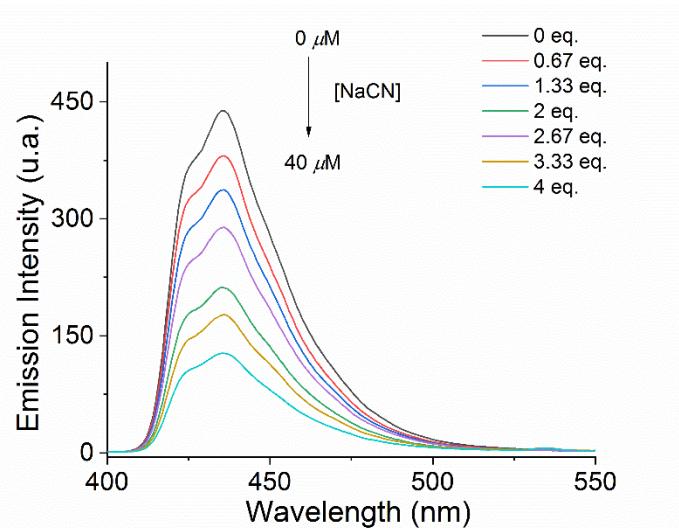


Fig. S16. Fluorescence response of **3** ($10 \mu\text{M}$) upon addition of CN^- at $\text{pH}=7.0$ in the presence of sodium salts of F^- , Cl^- , H_2PO_4^- , HCO_3^- , NO_3^- , H_2AsO_3^- and SO_4^{2-} (1.0 mM each).