A series of coordination networks constructed from the rigid ligand

4,4'-ethynylenedibenzoate: topological diversity, entanglement,

supramolecular interactions and photophysical properties

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Experimental Section

Synthesis of $Gd(NO_3)_3$, xH_2O . A suspension of Gd_2O_3 (0.50 g, 1.37 mmol) in 3 mL of distilled water was heated up to 100 °C under stirring. Then, 65% HNO₃ (0.55 mL, 8.00 mmol) was slowly added up to the solution became slightly turbid. The resulting mixture was filtered and the water rota-evaporated, yielding a white solid that was dried under vacuum (1.05 g, 2.5 mmol, 87%).

Synthesis of methyl 4,4'-ethynylenedibenzoate (1).¹ To a Schlenk flask containing $PdCl_2(PPh_3)_2$ (0.142 g, 0.20 mmol), CuI (0.118 g, 0.62 mmol) and methyl 4iodobenzoate (5.21 g, 0.02 mol) were added 20 mL of DBU and 40 mL of Et₃N. The solution was stirred under Ar for few seconds and then 1.4 mL of TMSA was added, followed immediately by the addition of 0.14 mL of H₂O. The solution was stirred at room temperature for 6 h. At the end, the solvent was removed under vacuum forming a brown residue to which was added water. This suspension was filtered, the solid washed with H₂O and recrystallized from EtOAc, affording the product as a white solid (2.17 g, 8.15 mmol, 81%). M.p.: 220–222 °C. FTIR v (cm⁻¹) 2956–2925 (C–H, m), 2844 (C–H, m), 1714 (C=O, vs), 1099 (C–O, s); ¹H NMR (500 MHz, CDCl₃) δ : 8.04 (d, *J* = 8.7 Hz, 4H), 7.60 (d, *J* = 8.7 Hz, 4H), 3.93 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ : 166.4, 131.6, 129.9, 129.6, 127.3, 91.3, 52.3. Elemental analysis calculated for C₁₈H₁₄O₄: C 73.46 %, H 4.79 %; experimentally determined: C 73.42 %, H 4.61 %.

Synthesis of 4,4'-ethynylenedibenzoic acid (H₂edb, 2).¹ Compound 1 (2.17 g, 8.15 mmol) was dispersed in 50 mL of a solution of solution of KOH (4.57 g, 81.5 mml) in EtOH:H₂O (9:1). The mixture was stirred overnight at 40 °C. The solvent was removed under vacuum and the solid was redissolved in H₂O and washed with CH₂Cl₂. Compound **2** was precipitated from the aqueous solution by adding 12 mol L⁻¹ HCl to the aqueous fraction. The white solid was collected by filtration and washed with H₂O

up to neutral pH (1.74 g, 6.5 mmol, 79%). H₂edb decomposes before melting at 350 °C. FTIR v (cm⁻¹) 3600–2200 (C–H, m), 2817 – 2660 (C–H, m), 2844 (C–H, m), 1673 (C=O, vs), 1175 (C–O, s); ¹H NMR (500 MHz, DMSO-*d*₆) δ : 7.99 (d, *J* = 8.51, 4H), 7.70 (d, *J* = 8.52, 4H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ : 166.4, 131.5, 130.8, 129.4, 125.9, 90.9. Elemental analysis calculated for C₁₆H₁₀O₄: C 72.18 %, H 3.79 %; experimentally determined: C 72.03 %, H 3.85 %.



Figure S1. FTIR spectrum of compound 2 (H₂edb).



Figure S2. FTIR spectra of compound 2 and the coordination networks 3, 4, 5 and 6.



Figure S3. Asymmetric unit of CN 3.

Atom 2	Distance Å
N1	2.183(4)
N2	2.180(3)
$O1_{\rm w}$	2.128(2)
01	2.074(2)
	Atom 2 N1 N2 O1 _w O1

Table S1. Selected bond distances for CN 3

 Table S2. List of main hydrogen bonds in CN 3 [Å, degree]

Donor (D)	Acceptor (A)	d(D····A)	d(D–H···A)	a(D-H···A)	Symmetry
O1 _W -H1 _{WB}	02	2.636(6)	1.646	173.06	1-x, y, 1/2-z
C4–H4	O2	3.607(6)	2.685	171.29	2-x, y, 1/2-z
C14–H14	O2	3.380(9)	2.645	136.18	-1/2+x, -1/2+y, z



Figure S4. Asymmetric unit of CN **4**. Hydrogen and disordered atoms were hidden for clarity.

Atom 1	Atom 2	Distance Å
Cd1	01	2.435(3)
Cd1	O2	2.363(2)
Cd1	03	2.272(3)
Cd1	O4	2.247(3)
Cd1	$O1_{D1}$	2.282(3)
Cd1	$O1_{D1}$	2.278(3)

Table S3. Selected bond distances for CN 4

Table S4. List of main hydrogen bonds interactions in CN 4 [Å, degree]

Donor (D)	Acceptor (A)	d(D····A)	d(D–H···A)	a(D–H···A)	Symmetry
С3–Н3	01	3.286(5)	2.364	170.26	
C1 _{D2} –H1 _{DB}	$O1_{D1}$	3.558(6)	2.605	171.88	x, -1+y, z
C4–H4	$S1_{D2}$	3.889(3)	2.989	163.42	x, 1-y, -1/2+z
$C2_{D2}$ -H2 _{DB}	02	3.307(6)	2.456	147.72	1/2-x, -1/2+y, 1/2-z
С6–Н6	Cg	3.656(4)	2.875	144.70	x, 1-y, 1/2+z

Note: The centroid Cg is formed by the carbons C10–C15.



Figure S5. Asymmetric unit of CN 5. Hydrogen and disordered atoms were hidden for clarity.

Atom 1	Atom 2	Distance Å
Er1	01	2.438(5)
Er1	02	2.388(5)
Er1	03	2.330(5)
Er1	O4	2.264(5)
Er1	O5	2.360(5)
Er1	$O1_{D1}$	2.250(5)
Er1	$O1_{w}$	2.354(5)
Er1	$O1_{D1}$	2.269(5)

 Table S5. Selected bond distances for CN 5.

Donor (D)	Acceptor (A)	d(D…A)	d(D–H···A)	a(D–H···A)	Symmetry
O1 _W -H1 _{WA}	05	2.7574(13)	1.9833	149.87	2-x, -1-y, -z
$O1_W$ – $H1_{WB}$	01	2.7130(13)	2.1175	126.27	2-x, 1-y, -1-z
$C4_{D1}$ – $H4_{DB}$	O5	2.8796(12)	2.5147	102.27	-1+x, y, z
С13-Н13	O2	3.4610(14)	2.6028	153.66	3-x, 1-y, -1-z

Table S6. List of main hydrogen bond interactions in CN 5. [Å, degree]



Figure S6. Asymmetric unit of CN 6. Hydrogen and disordered atoms were hidden for clarity.

Atom 1	Atom 2	Distance (Å)
Gd1	07	2.271(16)
Gd1	03	2.283(14)
Gd1	05	2.323(15)
Gd1	01	2.336(15)
Gd1	O10	2.436(13)
Gd1	$O1_{W1}$	2.45(3)
Gd1	$O1_{W2}$	2.466(19)
Gd1	09	2.563(16)
Gd2	O6	2.286(15)
Gd2	02	2.330(17)
Gd2	O4	2.348(17)
Gd2	$O1_{W4}$	2.37(4)
Gd2	08	2.369(14)
Gd2	011	2.38(2)
Gd2	O1 _{W3}	2.41(2)

 Table S7. Selected bond distances for CN 6

Table S8. List of main interactions in CN 6 [Å, degree]

3.23(3)	1/2-x $1/2+y$ 1 $5-z$
3 · _ = (•)	$1/2$ A, $1/2 \cdot y$, $1.5 \cdot z$
3.48(6)	1/2-x, 1/2+y, 1.5-z
	3.48(6)



Figure S7. Powder X-ray diffraction patterns for 3 (a), 4 (b), 5 (c), and 6 (d).



Figure S8. Thermogravimetric analyses of the compounds: a) compound 2; b) compound 3; c) compound 4; d) compound 5, and e) compound 6.



Figure S9. Fluorescence lifetime measurements. (a) Measured decay for 2 ($\lambda_{em} = 385$ nm), (b) decay fitting for 2 ($\lambda_{em} = 385$ nm), (c) measured decay for CN 4 ($\lambda_{em} = 444$ nm), (d) fitting decay for CN 4 ($\lambda_{em} = 444$ nm), (e) measured decay for CN 4 ($\lambda_{em} = 586$ nm), (f) fitting decay for 4 ($\lambda_{em} = 586$ nm).

References

 T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 31, 3672.