Supporting Information

Novel Near-IR Absorbing Phenyl-Substituted Phthalo- and Naphthalocyanine Complexes of Lanthanide (III): Synthesis, Spectral and Electrochemical Properties

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Table S1. High-resolution mass spectrometry MALDI TOF/TOF data.

Compound (Molecular formula)	Mass found	Monoisotopic mass calculated
5a ($C_{160}H_{97}EuN_{16}$)	2394.8547	2394.7294
5b ($C_{160}H_{100}ErN_{16}$)	2410.7451	2410.7620
5c ($C_{160}H_{98}LuN_{16}$)	2417.7568	2417.7915
6a ($C_{240}H_{145}Eu_2N_{24}$)	3668.9224	3668.0509
6b ($C_{240}H_{150}Er_2N_{24}$)	3699.8464	3699.1081
6c ($C_{240}H_{146}Lu_2N_{24}$)	3712.9421	3713.0978
11a ($C_{192}H_{114}EuN_{16}$)	2795.4863	2795.8625
11b ($C_{192}H_{116}ErN_{16}$)	2810.3835	2810.8872
11c ($C_{192}H_{115}LuN_{16}$)	2818.3562	2818.8898

Table S2. Spectral and electrochemical data for substituted diphthalocyanine lutetium complexes in *o*-DCB.

	$\Delta E^{o'}(Ox_2)$-(Ox_1)	$\Delta E^{o'}(Red_1)$-(Red_2)	IV band/nm (CCl_4)
$^{\alpha\text{-}C5H11O}Pc_2Lu$[21]	0.95	1.20	1666
$^{Bu}Pc_2Lu$[22]	1.20	1.09	1453
$^{Et}Pc_2Lu$[22]	1.20	1.09	1445
$^{Ph}Pc_2Lu$ (5c)	1.23	1.02	1393

Table S3. Crystal data and structure refinement for diphthalocyanine **5c**.

Empirical formula	C260 H497 Lu N16 O100.50
Formula weight [g mol^{-1}]	5630.68
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Tetragonal
Space group	P 4/n
a [Å]	31.3930(10)
b [Å]	31.3930(10)
c [Å]	10.6224(7)
α [°]	90
β [°]	90
γ [°]	90
Volume $[Å]^3$	10468.6(8)
Z	2
Density (calculated) $[Mg/m^3]$	0.770
Absorption coefficient [μ, mm^{-1}]	0.509
F(000)	2488
Crystal size $[mm^3]$	0.550 x 0.430 x 0.150
Theta range for data collection [°]	3.29 to 29.00
Index ranges	$-42 \le h \le 42$, $-42 \le k \le 42$, $-14 \le l \le 14$
Reflections collected	122224
Independent reflections	13811 [R(int) = 0.0897]
Completeness to theta = 29.00°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.916 and 0.761
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13811 / 0 / 402
Goodness-of-fit on F^2	0.998
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1145
R indices (all data)	R1 = 0.0689, wR2 = 0.1222
Largest diff. peak and hole $[e/Å]^{-3}$	3.580 and -1.415

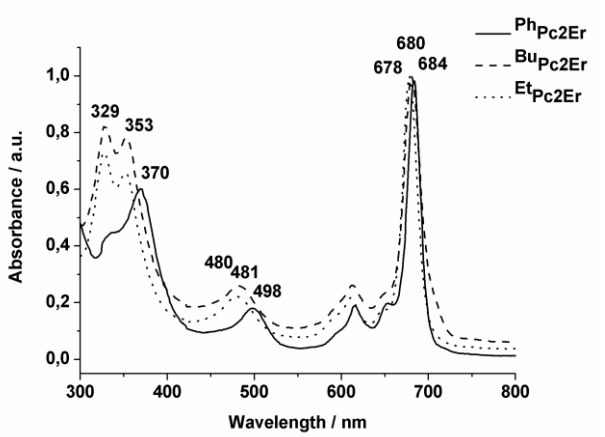

Figure S1. UV-Vis spectra of diphthalocyanines **5b** ($^{Ph}Pc_2Er$), octa-butyl substituted diphthalocyanine erbium ($^{Bu}Pc_2Er$) and octa-ethyl substituted diphthalocyanine erbium ($^{Et}Pc_2Er$) in $CHCl_3$.

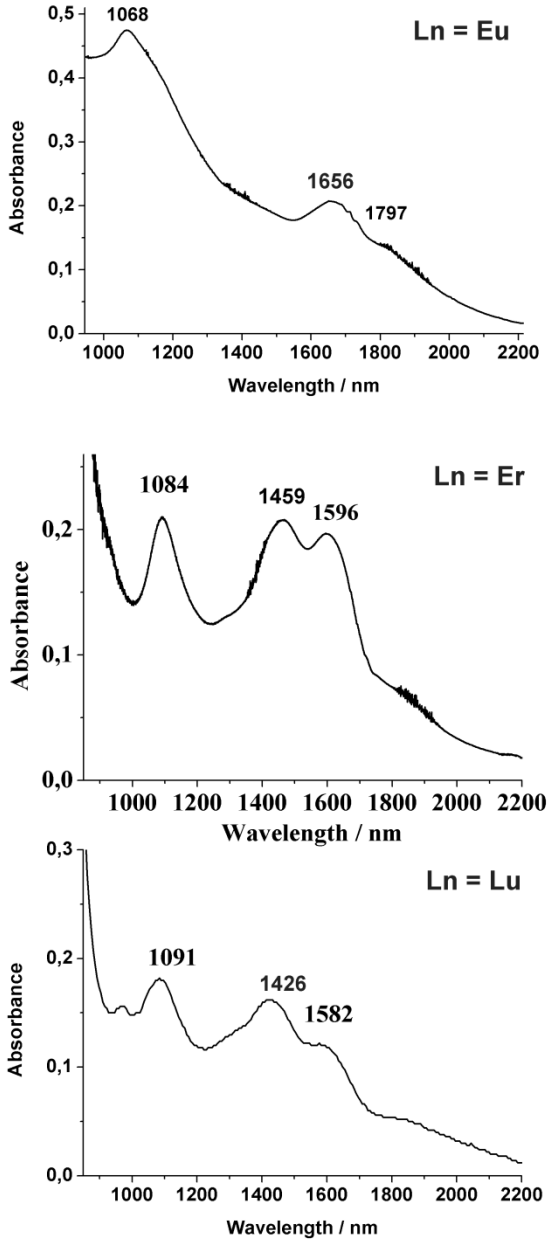

Figure S2. Near-IR spectra of dinaphthalocyanines **11a-c** in CCl_4.

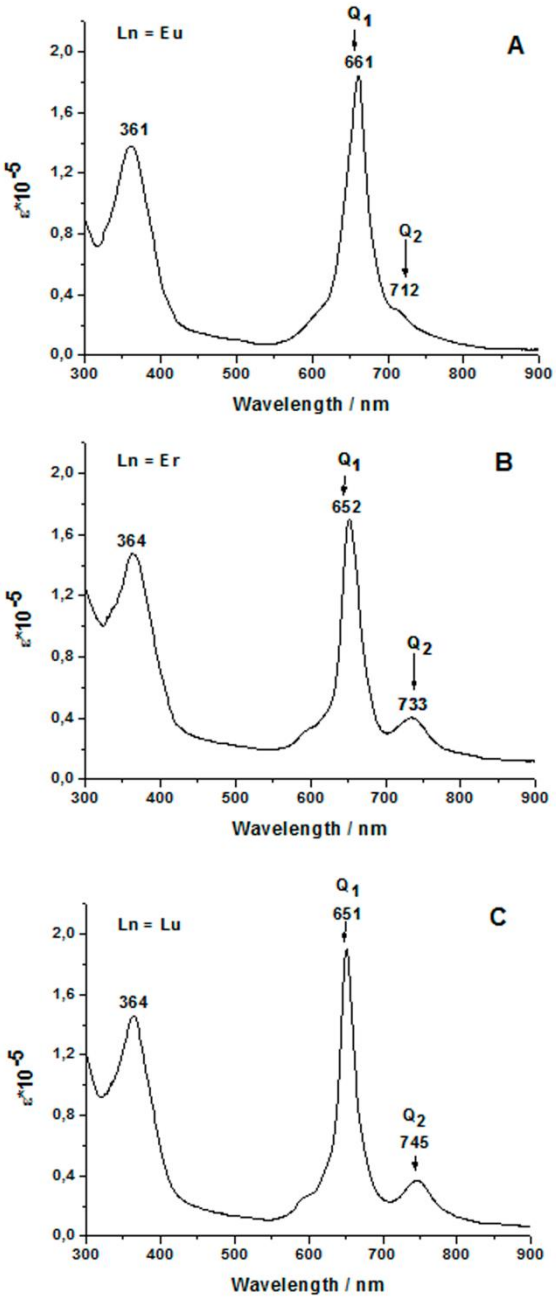

Figure S3. UV/Vis spectra of triple-decker **6a-c** complexes in THF.

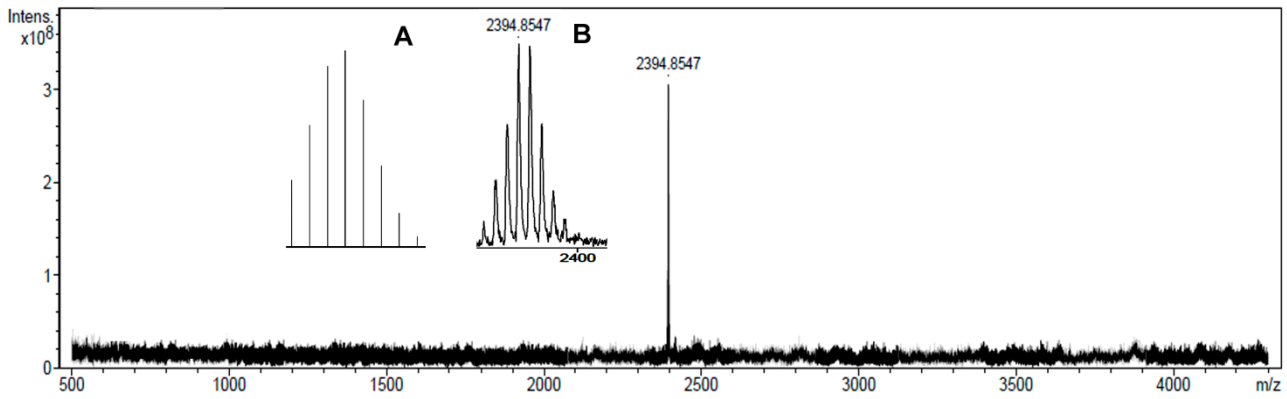

Figure S5. High-resolution MALDI-TOF/TOF mass spectrum of **5a**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

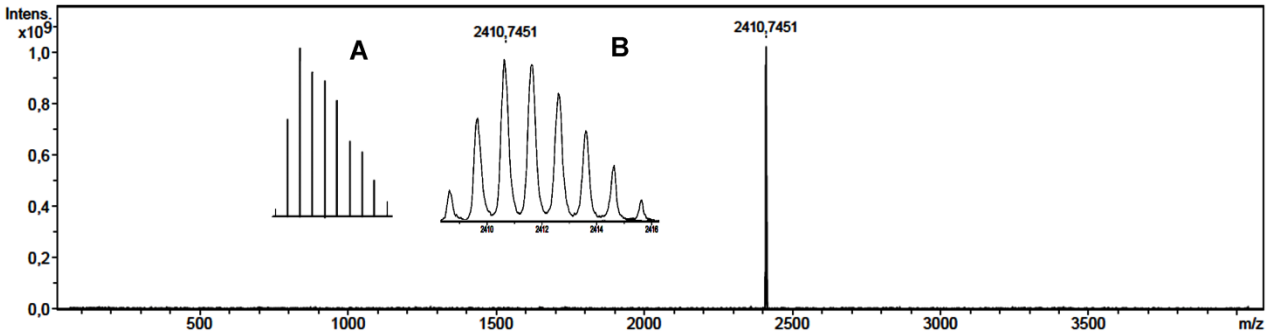

Figure S6. High-resolution MALDI-TOF/TOF mass spectrum of **5b**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

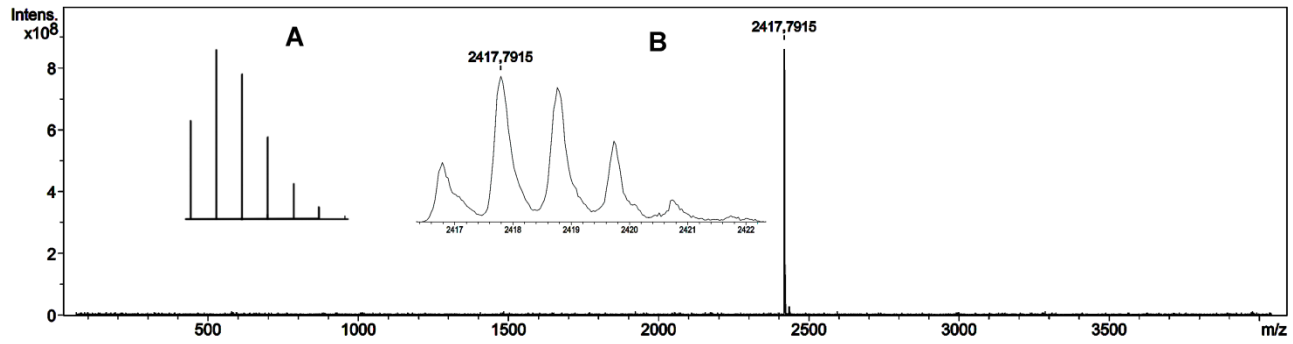

Figure S7. High-resolution MALDI-TOF/TOF mass spectrum of **5c**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

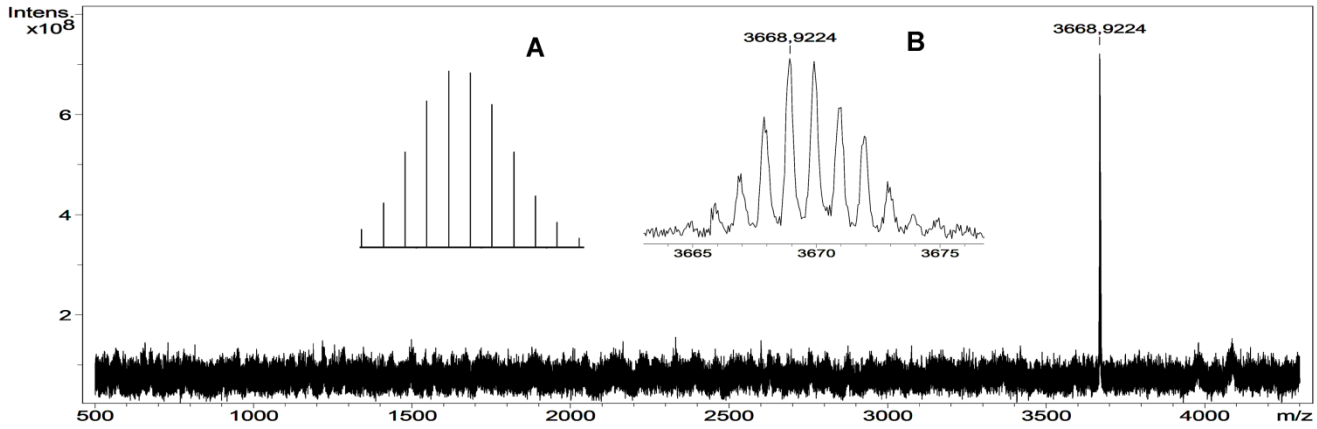

Figure S8. High-resolution MALDI-TOF/TOF mass spectrum of **6a**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

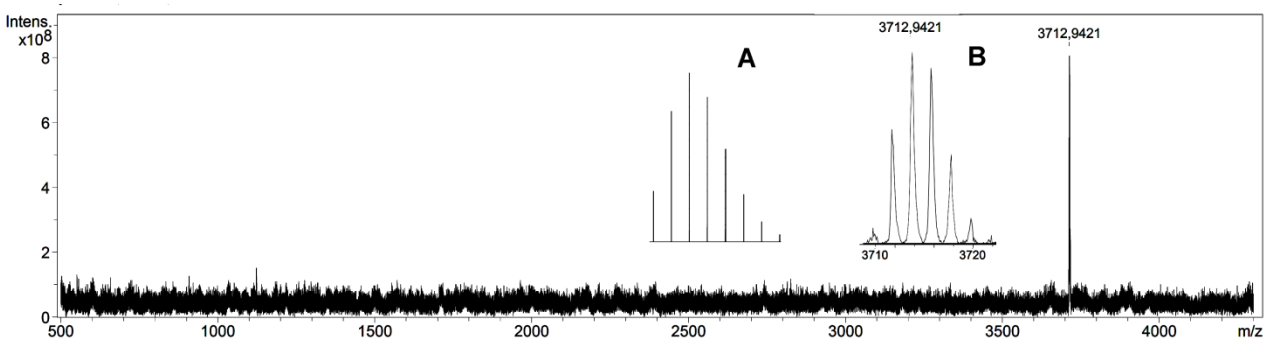

Figure S9. High-resolution MALDI-TOF/TOF mass spectrum of **6c**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

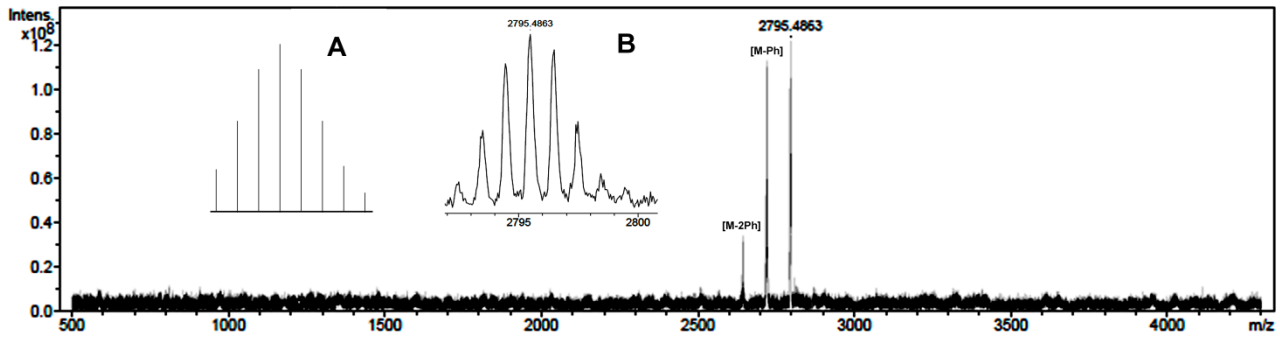

Figure S10. High-resolution MALDI-TOF/TOF mass spectrum of **11a**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

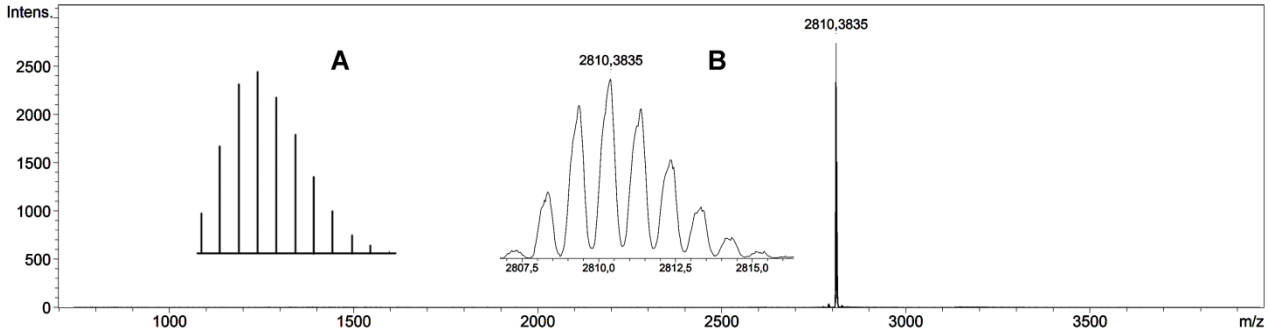

Figure S11. High-resolution MALDI-TOF/TOF mass spectrum of **11b**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

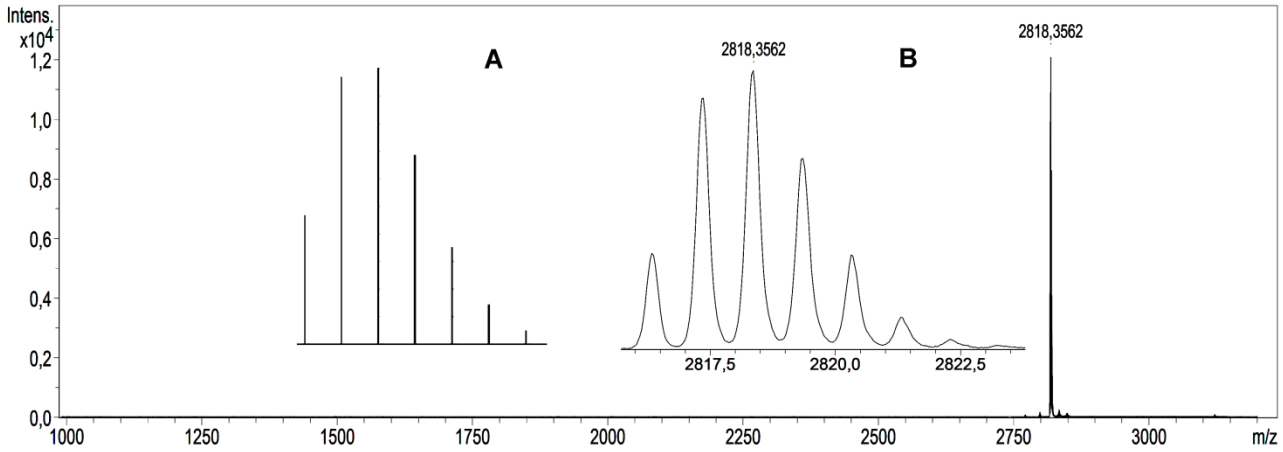

Figure S12. High-resolution MALDI-TOF/TOF mass spectrum of **11c**, isotopic patterns for the molecular ion (inset B) and simulated MS patterns of the molecular ion (inset A).

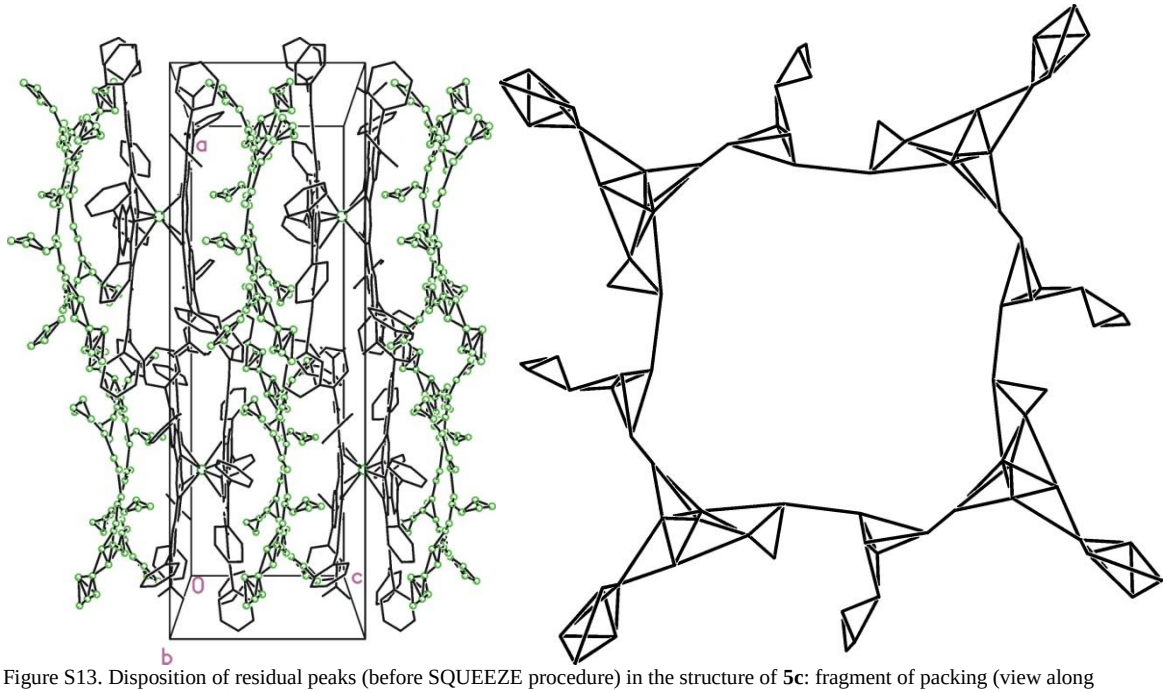

Figure S13. Disposition of residual peaks (before SQUEEZE procedure) in the structure of **5c**: fragment of packing (view along crystallographic axis b, left) and residual peaks view perpendicular to the q4-q30 plane.

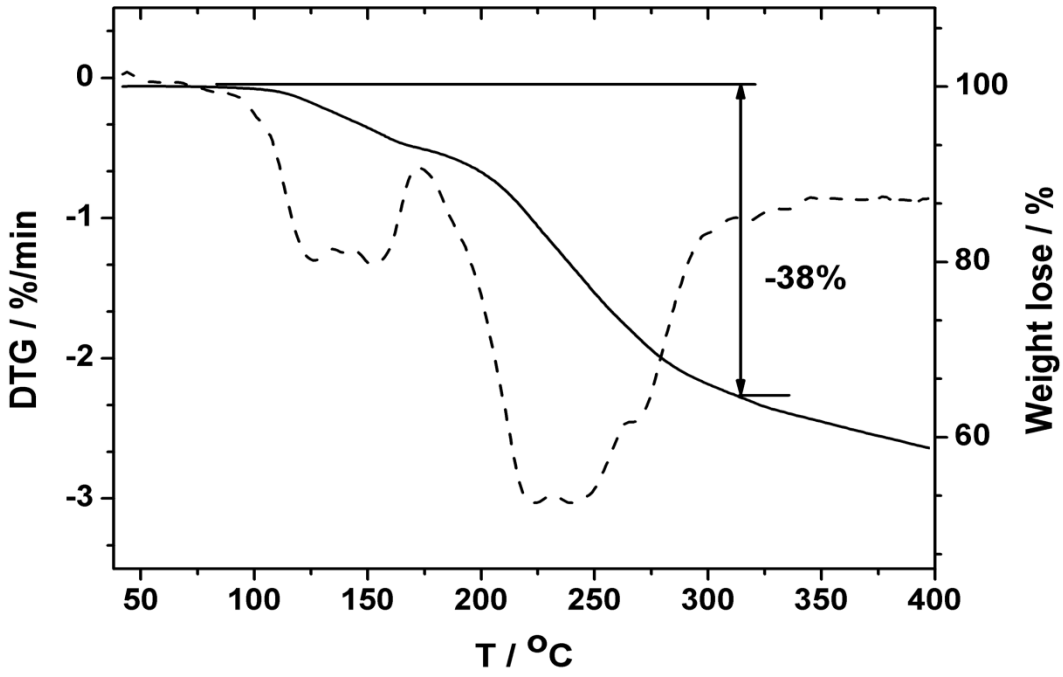

Figure S14. TGA (solid line) and DTG (dashed line) curves for complex **5c**.