Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Data

Structure characterization of non-crystalline complexes of copper salts with native cyclodextrins.

Manuel I. Velasco,[a] Claudio R. Krapacher,[a] Rita Hoyos de Rossi,[a] Laura I. Rossi.[a*]

[a] Instituto de Investigaciones en Físico Química de Córdoba (INFIQC) - CONICET, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria. X5000HUA Córdoba, Argentina.

* Corresponding author

[a] (INFIQC-CONICET) Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria. X5000HUA Córdoba, Argentina. Tel: +54-351-5353867. E-mail address: mvelasco@fcq.unc.edu.ar (Manuel I. Velasco); ckrapacher@fcq.unc.edu.ar (Claudio R. Krapacher); ritah@fcq.unc.edu.ar (Rita Hoyos de Rossi); lauraros@fcq.unc.edu.ar (Laura I. Rossi)*

Figure 1S: TGA of αCD $CuCl_2$ complex

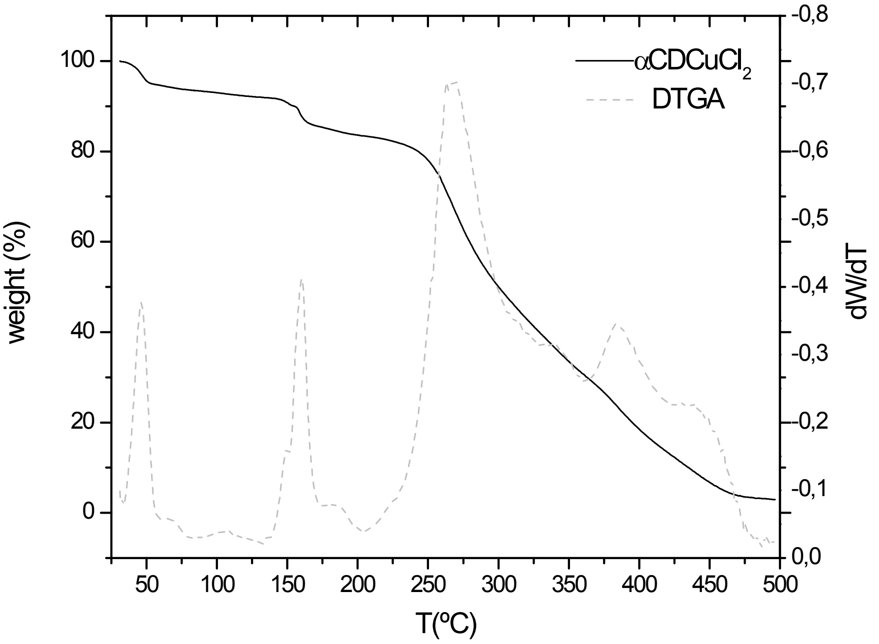


Figure 2S: RD UV-Vis of αCD $CuCl_2$ complex

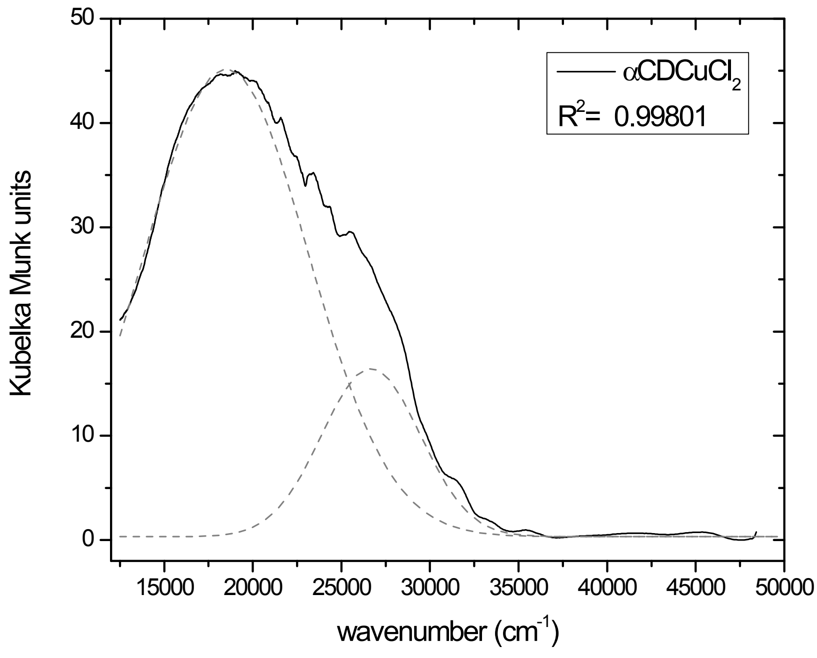


Figure 3S: TGA of βCD $CuCl_2$ complex

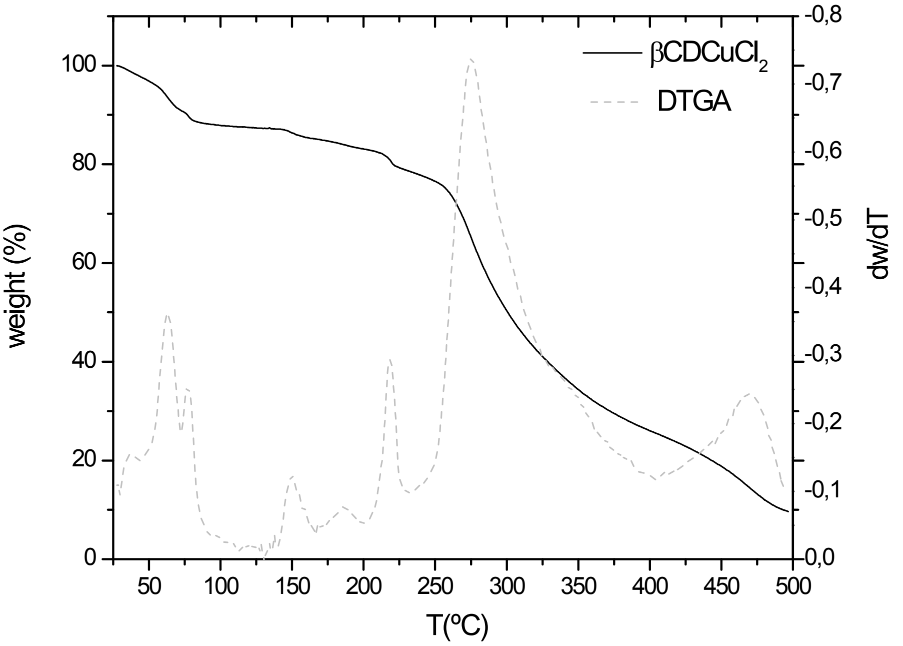


Figure 4S: RD UV-Vis of βCD $CuCl_2$ complex

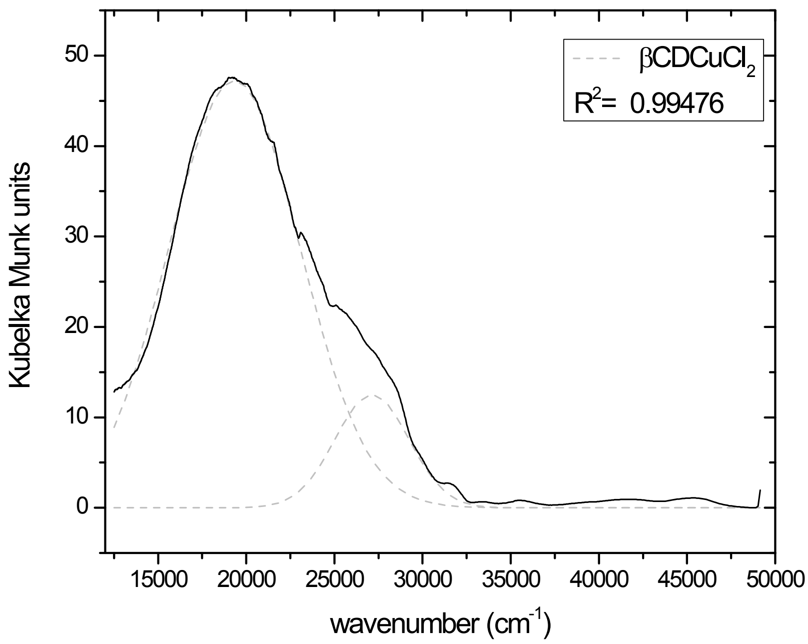


Figure 5S: TGA of γCD $CuCl_2$ complex

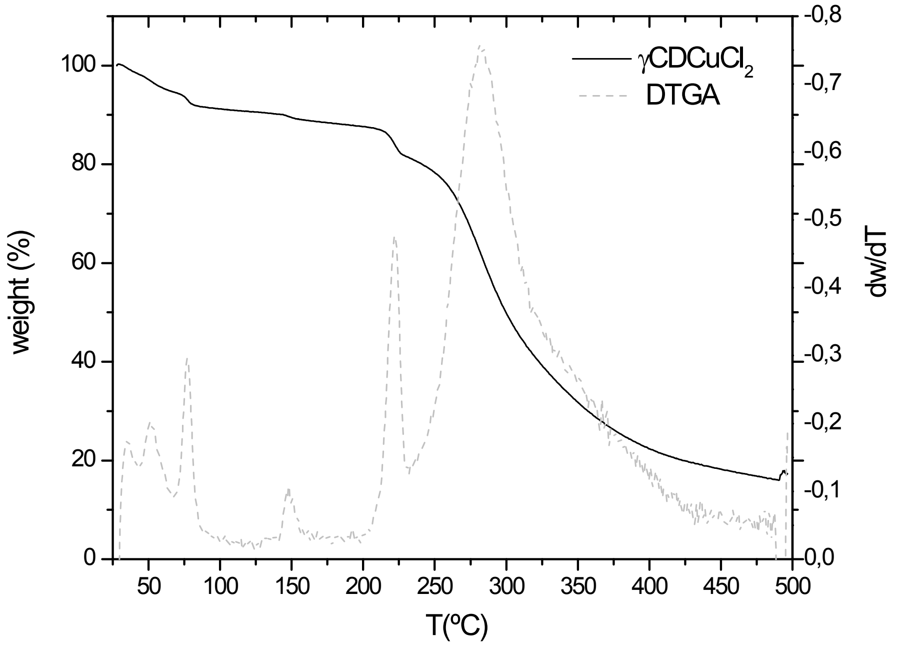


Figure 6S: RD UV-Vis of γCD $CuCl_2$ complex

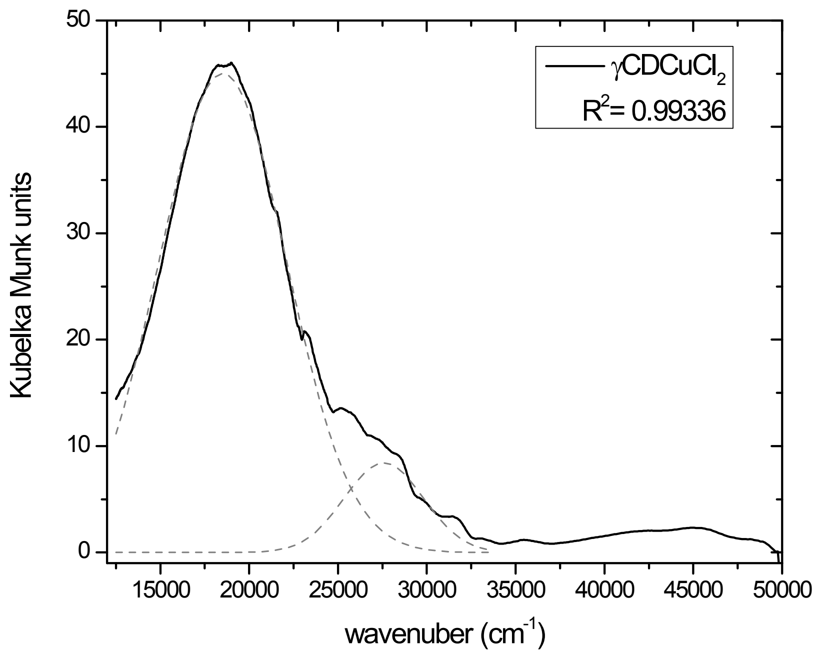


Figure 7S: TGA of αCD $Cu(NO_3)_2$ complex

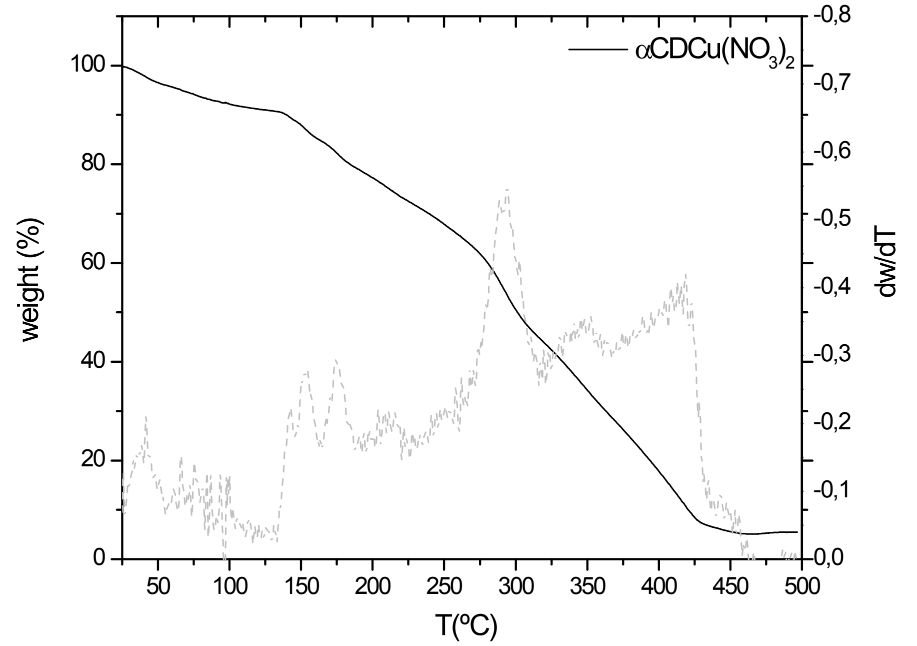


Figure 8S: RD UV-Vis of αCD $Cu(NO_3)_2$ complex

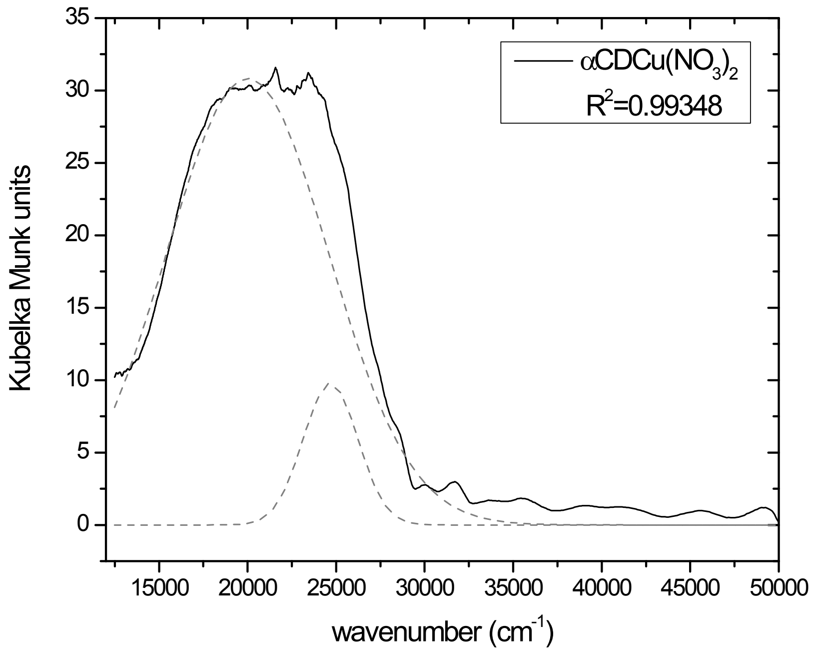


Figure 9S: TGA of βCD $Cu(NO_3)_2$ complex

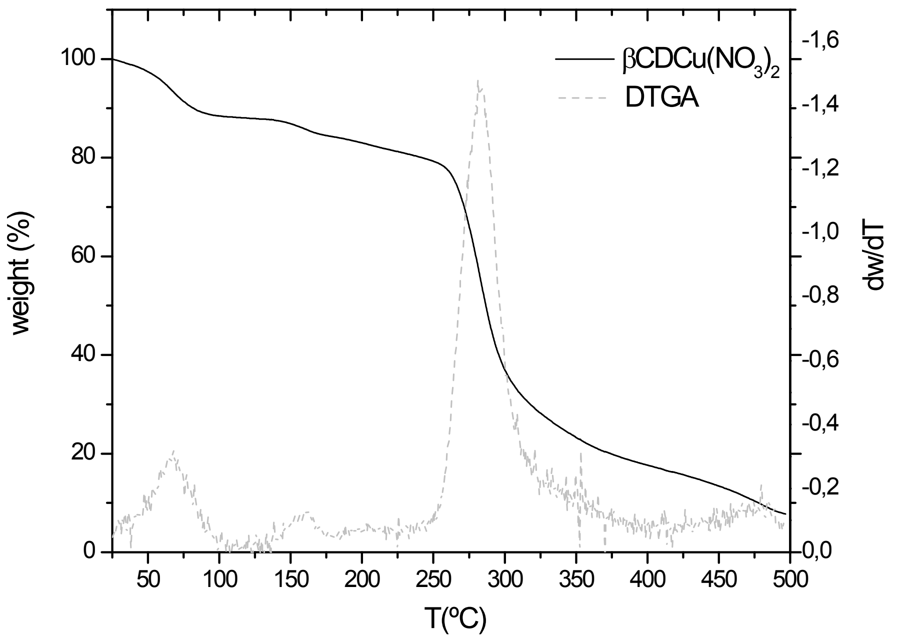


Figure 10S: RD UV-Vis of βCD $Cu(NO_3)_2$ complex

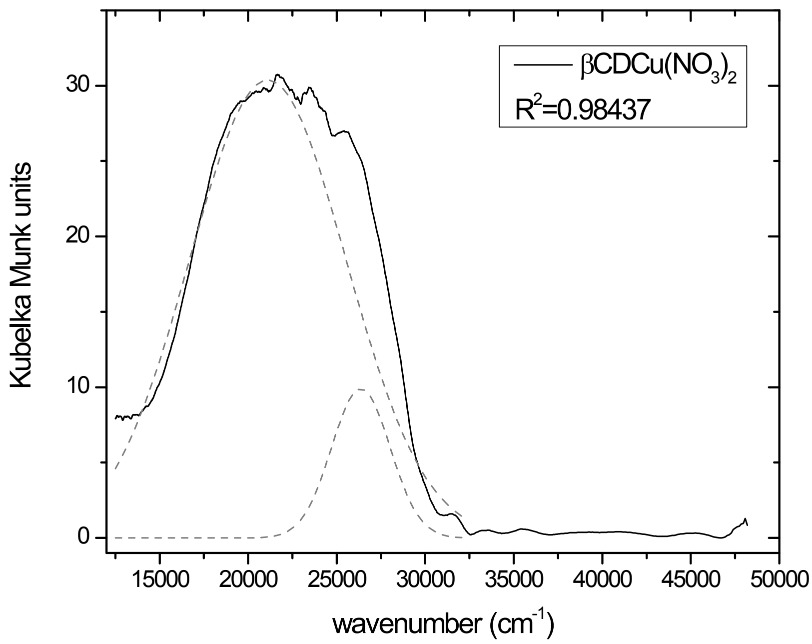


Figure 11S: TGA of γCD $Cu(NO_3)_2$ complex

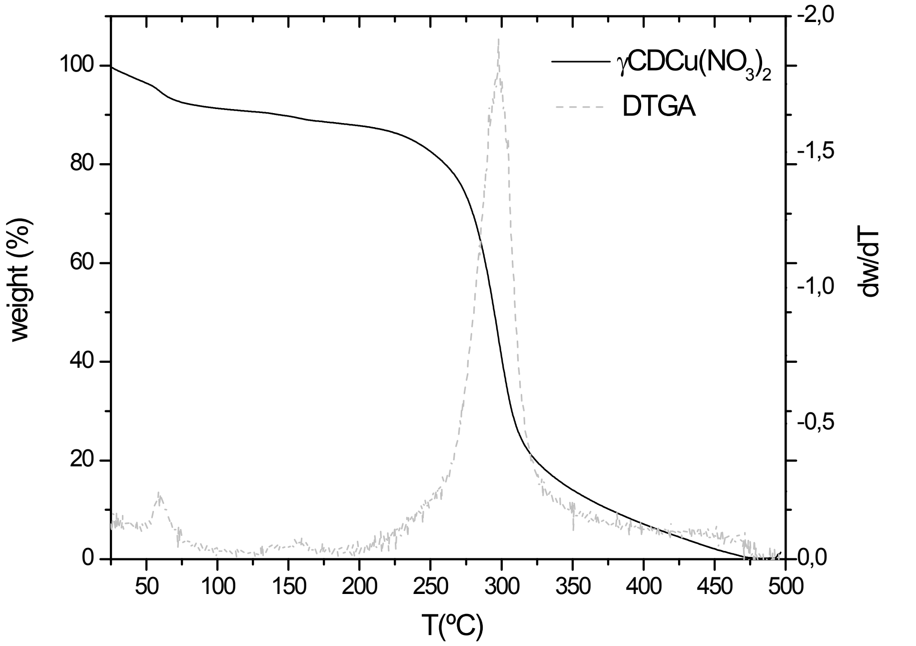


Figure 12S: RD UV-Vis of γCD $Cu(NO_3)_2$ complex

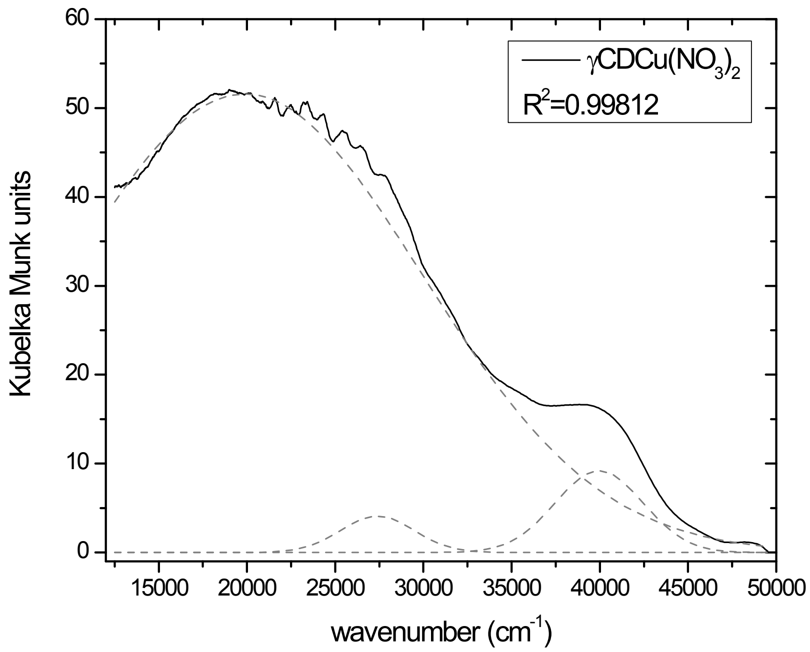


Figure 13S: TGA of βCDCuBr$_2$ complex

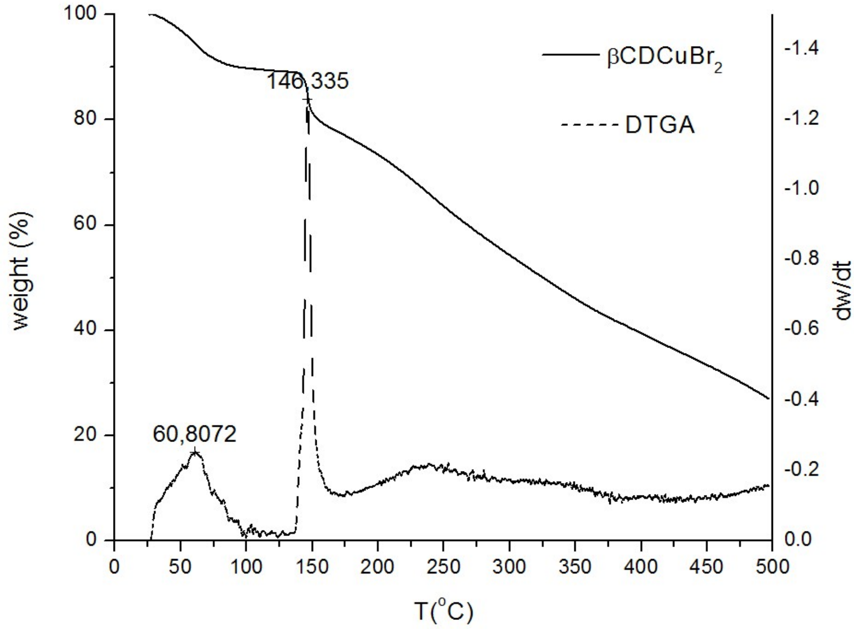


Figure 14S: RD UV-Vis of βCDCuBr$_2$ complex

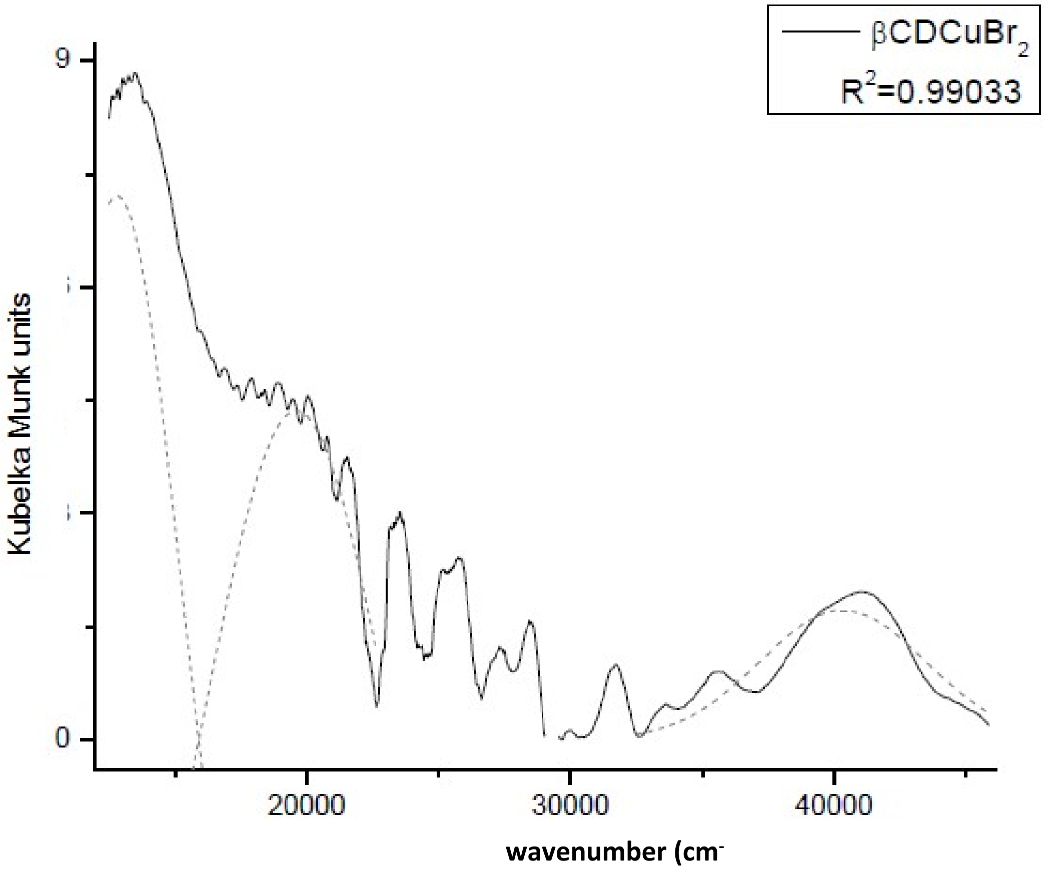


Figure 15S: TGA of γCDCuBr$_2$ complex

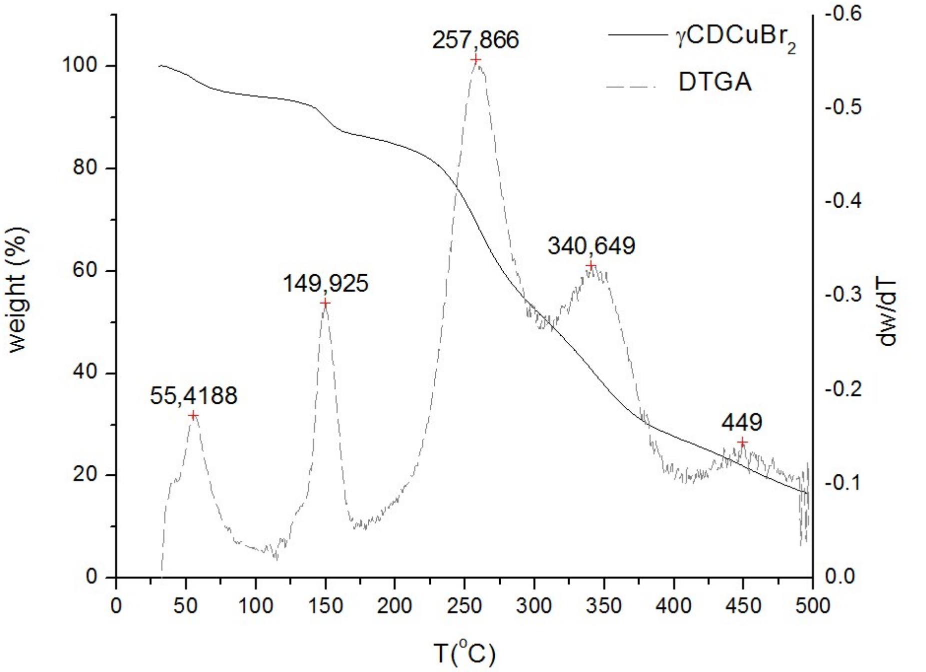


Figure 16S: RD UV-Vis of γCDCuBr$_2$ complex

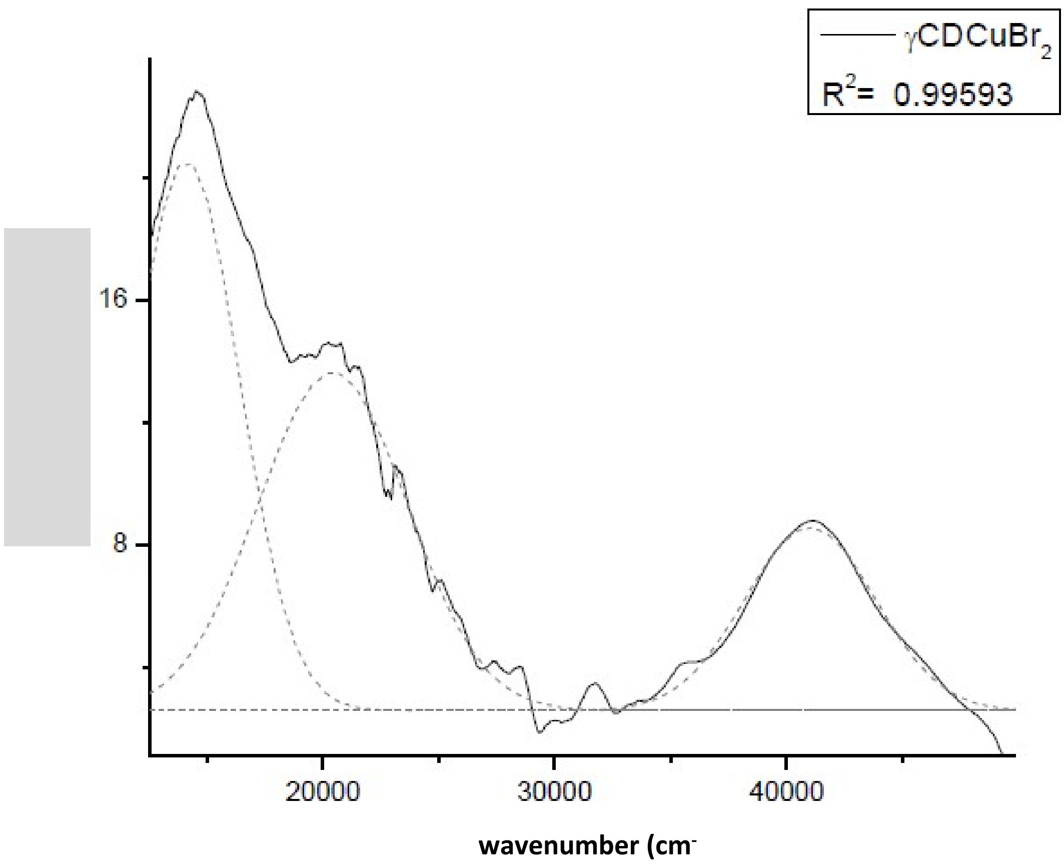


Table 1S: Elemental analysis results and complementary studies.

Native or Complex CDs	M_w [a] (EA_w) [b]	Formula	Elemental Analysis % found ; % calculated		
			C	H	Metal
αCD	5.8 [6-7] [c]	$C_{36}H_{60}O_{30}$	--;44.45	--;6.22	--
βCD	7.4 [11-12] [c]	$C_{42}H_{70}O_{35}$	--;44.45	--;6.22	--
γCD	6.0 [17] [c]	$C_{48}H_{80}O_{40}$	--;44.45	--;6.22	--
$\alpha CDCuCl_2$	7.5 (6)	$xH_2O \cdot (C_{36}H_{60}O_{30}) \cdot (CuCl_2)$	39.34; 35.58	4.26; 5.97	4.02; 5.22
$\beta CDCuCl_2$	8.3 (9)	$xH_2O \cdot (C_{42}H_{70}O_{35}) \cdot (CuCl_2)$	34.76; 35.24	5.92; 6.20	4.90; 4.44
$\gamma CDCuCl_2$	8.6 (11)	$xH_2O \cdot (C_{48}H_{80}O_{40}) \cdot (CuCl_2)$	34.54; 35.37	6.03; 6.31	4.02; 3.90
$\alpha CDCuBr_2$	9.4 (6)	$xH_2O \cdot (C_{36}H_{60}O_{30}) \cdot (CuBr_2)$	35.83; 35.57	3.93; 5.91	4.09; 5.11

[a] M_w: Mol of water per mole of cyclodextrin by TGA.

[b] (EA_w) = Mol of water per mole of cyclodextrin by elemental analysis.

[c] Reference 44

Table 2S: Kinetic parameters of the thermal decomposition of natives CD and their complexes.

Native CD or Complex[a]	Decomposition Temperature (K) (DTGA max or average; weight %)	E* (kJ·mol^{-1})	A (s^{-1}) (logA)	ΔS* (kJ·mol^{-1}·K^{-1})	ΔH* (kJ·mol^{-1})	ΔG* (kJ·mol^{-1})
αCD 1.6140x10^{-3}g 1.660x10^{-6}mol	313 – 323 (323;97.69)	144.38	7.10x10^{19} (19.85)	0.13	141.69	98.25
	337 – 349 (344;93.47)	44.42	1.33x10^{3} (3.13)	-0.19	41.56	105.67
	559 – 593 (581;52.98)	162.80	1.26x10^{12} (12.11)	-0.02	157.97	168.91
βCD 2.5350x10^{-3}g 2.233x10^{-6}mol	313 – 343 (336;94.79)	51.45	2.26x10^{4} (4.35)	-0.16	48.66	103.29
	345 – 359 (353;89.63)	28.80	4.36 (0.64)	-0.23	25.86	108.05
	593 – 613 (600;55.40)	332.09	4.01x10^{26} (26.63)	0.26	327.10	171.93
γCD 1.6130x10^{-3}g 1.244x10^{-6}mol	313 – 339 (337;95.75)	44.04	1.11x10^{3} (3.05)	-0.19	41.24	104.49
	341 – 351 (346;94.40)	18.96	6.32x10^{-2} (-1.20)	-0.27	16.08	109.21
	565 – 597 (583;56.93)	222.85	3.02x10^{17} (17.50)	0.08	218.00	168.93
αCDCuCl$_2$ 1.1170x10^{-3}g 1.009x10^{-6}mol	311 - 321 (319;97.22)	146.04	2.86x10^{20} (20.46)	0.15	143.39	96.76
	419 - 423 (421;91.12)	20.30	3.17x10^{-2} (-1.50)	-0.28	16.80	133.22
	429 - 435 (433;87.87)	63.09	1.57x10^{4} (4.20)	-0.17	59.49	132.11
	523 - 563 (541;67.67)	49.59	3.61x10^{1} (1.56)	-0.22	45.10	164.17
	563 - 653 (608;38.13)	17.60	1.35x10^{-2} (-1.87)	-0.29	12.54	186.81
	653 - 713 (658;23.34)	28.55	1.65x10^{-1} (-0.78)	-0.27	23.08	198.46
βCDCuCl$_2$ 1.2840x10^{-3}g 1.011x10^{-6}mol	321 – 331 (326;96.31)	39.10	2.46 x10^{2} (2.39)	-0.20	36.39	101.57
	331 – 349 (345;90.93)	16.76	4.44 x10^{-2} (-1.35)	-0.27	13.89	107.76
	419 – 425 (422;86.47)	7.24	4.54 x10^{-4} (-3.35)	-0.31	3.74	135.34
	457 – 465 (458;84.04)	1.39	1.61 x10^{-5} (-4.96)	-0.34	-2.42	153.44
	487 – 495 (491;80.95)	25.98	1.30 x10^{-1} (-0.87)	-0.27	21.90	152.54
	533 – 563 (548;65.24)	52.41	73.02 (1.87)	-0.21	47.85	165.32
γCDCuCl$_2$ 0.6440x10^{-3}g 4.499x10^{-7}mol	313 – 329 (325;96.71)	53.65	7.30 x10^{4} (4.86)	-0.15	50.95	100.53
	347 – 353 (350;93.04)	38.24	1.19 x10^{2} (2.08)	-0.21	35.33	107.62
	417 – 423 (421;89.60)	8.31	5.79 x10^{-4} (-3.24)	-0.31	4.81	135.25
	489 – 497 (494;84.46)	53.00	1.56 x10^{2} (2.20)	-0.21	48.89	151.24
	533 – 573 (555;61.99)	54.53	125.80 (2.10)	-0.21	49.92	166.43

$\alpha CDCuBr_2$ $1.1140x10^{-3}$g $9.313x10^{-7}$mol	311 - 319 (318;98.37)	176.81	$2.75x10^{25}$ (25.44)	0.24	174.17	97.34
	337 - 345 (343;94.70)	38.91	$1.36x10^{2}$ (2.13)	-0.21	36.06	106.46
	413 - 419 (417;86.95)	73.49	$8.36x10^{5}$ (5.93)	-0.13	70.02	126.05
	503 – 543 (522;67.09)	26.62	$1.62x10^{-1}$ (-0.79)	-0.26	22.28	160.49
	573 – 723 (605;41.17)	19.42	$2.08x10^{-2}$ (-1.68)	-0.28	14.39	185.65
$\beta CDCuBr_2$ $1.1300x10^{-3}$g $8.319x10^{-7}$mol	311 – 327 (319;97.5)	58.94	$7.56 x10^{5}$ (5.88)	-0.13	56.29	98.70
	417 – 421 (420;83.74)	122.80	$2.85 x10^{12}$ (12.47)	$-0.93 x10^{-2}$	119.31	123.23
$\gamma CDCuBr_2$ $1.4360x10^{-3}$g $9.444x10^{-7}$mol	317 – 333 (329;97.44)	67.80	$9.67 x10^{6}$ (6.99)	-0.11	65.07	101.93
	415 – 431 (423;89.92)	34.20	3.55 (0.55)	-0.24	30.68	131.08
	513 - 543 (532;68.91)	42.05	8.11 (0.91)	-0.23	37.63	161.25
	603 – 643 (623;37.71)	23.55	$6.84 x10^{-2}$ (-1.17)	-0.27	18.37	188.70
$\alpha CDCu(NO_3)_2$ $1.1100x10^{-3}$g $9.566x10^{-7}$mol	307 - 315 (314;97.80)	74.43	$3.70x10^{8}$ (8.57)	-0.08	71.82	97.35
	323 - 353 (338;95.29)	13.85	$7.58x10^{-3}$ (-2.12)	-0.29	11.04	107.92
	409 - 429 (426;87.16)	21.94	$2.74x10^{-2}$ (-1.57)	-0.28	18.40	136.77
	441 - 459 (449;81.98)	18.39	$2.29x10^{-2}$ (-1.64)	-0.28	14.66	140.27
	543 - 583 (565;54.56)	27.29	$1.62x10^{-1}$ (-0.80)	-0.27	22.59	172.55
	683 - 701 (690;11.44)	83.85	$9.34 x10^{3}$ (3.97)	-0.18	78.11	199.50
$\beta CDCu(NO_3)_2$ $1.6010x10^{-3}$g $1.211x10^{-6}$mol	307 – 347 (340;93.55)	46.84	$3.98x10^{3}$ (3.60)	-0.18	44.01	104.24
	423 – 439 (433;85.81)	6.18	$2.68x10^{-4}$ (-3.57)	-0.32	2.58	139.62
	535 – 573 (556;55.34)	91.49	$6.55x10^{5}$ (5.82)	-0.14	86.87	164.03
$\gamma CDCu(NO_3)_2$ $1.0890x10^{-3}$g $7.335x10^{-7}$mol	309 – 337 (333;94.65)	31.58	$1.23 x10^{1}$ (1.09)	-0.23	28.81	103.75
	427 – 435 (431;89.31)	2.17	$2.11 x10^{-5}$ (-4.68)	-0.34	-1.41	144.08
	553 – 583 (571;44.54)	111.90	$4.11 x10^{7}$ (7.62)	-0.10	107.15	166.87

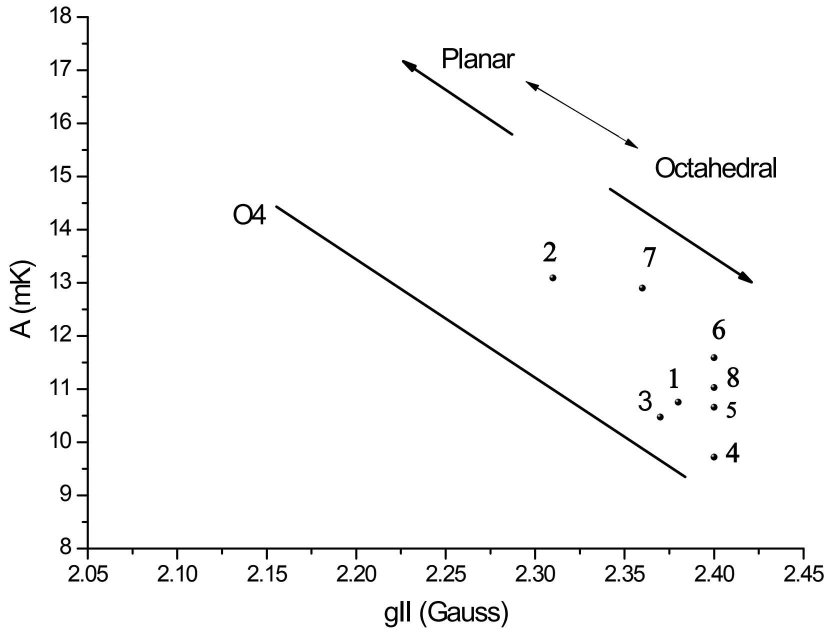
[a] Mol amount was calculated considerate anhydrous native CD or anhydrous complex

Table 3S: Activation energies of the thermal decomposition processes of native CDs and their complexes.

Natives CD or their complexes	Temperature Range			
	(313-383) K	(383-473) K	(473-623) K	(313-623) K
	E* (kJ/mol)			E* (kJ/mol)[a]
αCD	188.8	--	162.8	351.6
βCD	80.25	--	332.09	412.34
γCD	63	--	222.85	285.84
$\alpha CDCuCl_2$	146.04	83.39	67.19	296.62
$\beta CDCuCl_2$	55.86	8.63	78.39	142.88
$\gamma CDCuCl_2$	91.88	8.31	107.53	207.74
$\alpha CDCuBr_2$	215.72	73.49	46.04	335.25
$\beta CDCuBr_2$	58.94	122.8	--	181.74
$\gamma CDCuBr_2$	67.8	34.2	65.6	167.6
$\alpha CDCu(NO_3)_2$	88.28	40.33	27.29	155.9
$\beta CDCu(NO_3)_2$	46.84	6.18	91.49	144.5
$\gamma CDCu(NO_3)_2$	31.57	2.17	111.9	145.65

[a] These values were calculated from the sum of E* of the successive process

Figure 17S: Relationship between $A_{||}$ *vs* $g_{||}$ for $d_{x^2-y^2}$ Cu^{2+} ground state, Peisach-Blumberg correlation diagram.[a]



[a] The lines correspond to interaction of a metallic center with 4 oxygen atoms. See S.K. Hoffmann, J. Goslar, S. Lijewski, K. Tadyszak, A. Zalewska, A. Jankowska, P. Florczak, S. Kowalak. *Micropor. Mesopor. Mater.*, 2014, **186**, 57-64.

Figure 18S: Experimental and simulated EPR spectra of αCDCuCl_2.

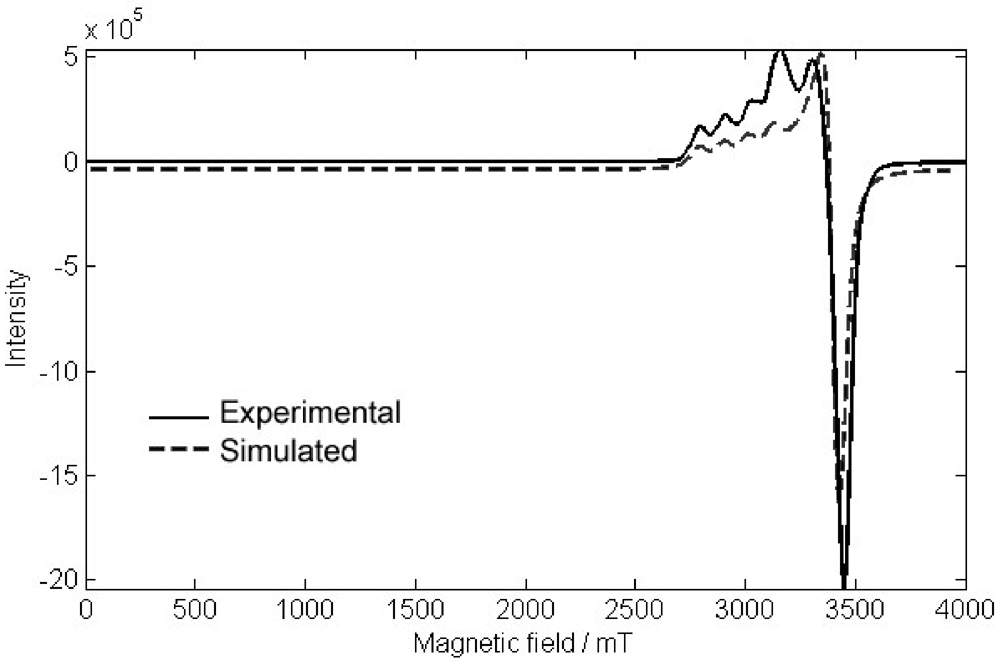


Figure 19S: Experimental and simulated EPR spectra of $\gamma CDCuCl_2$.