Synthesis of novel TEMPO stable free (poly)radical derivatives and their host-guest interaction with cucurbit[6]uril

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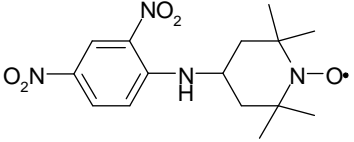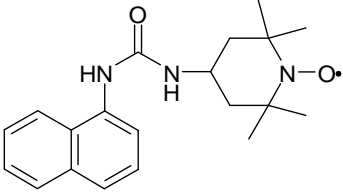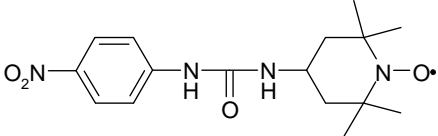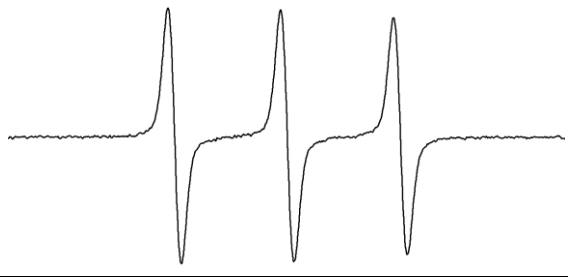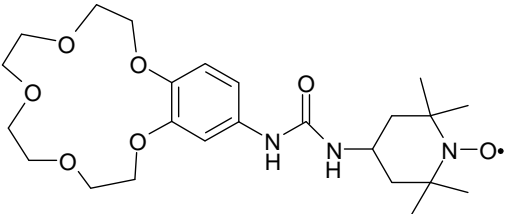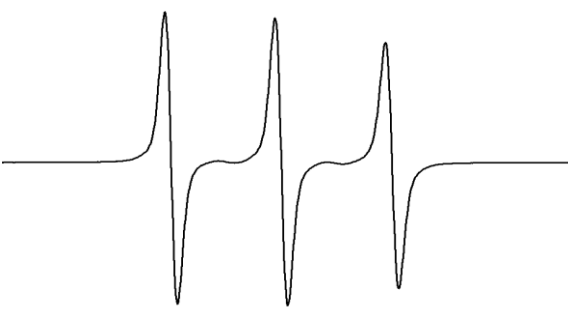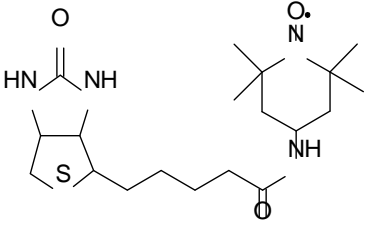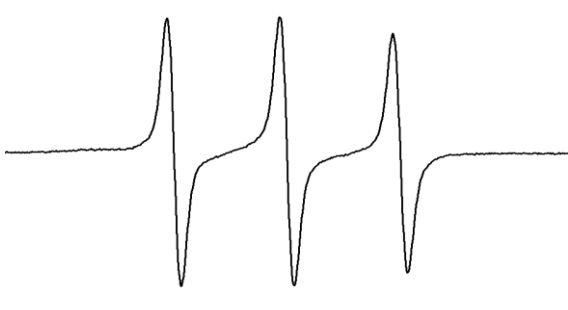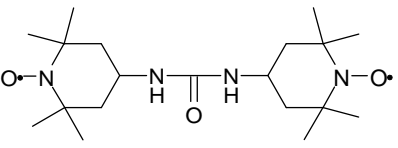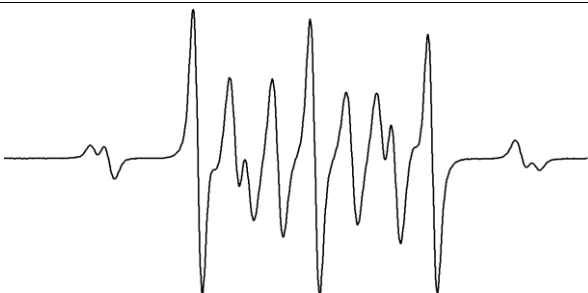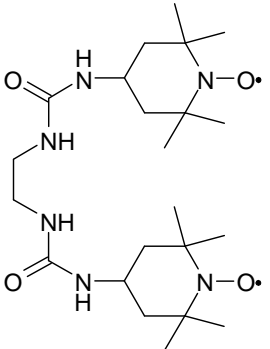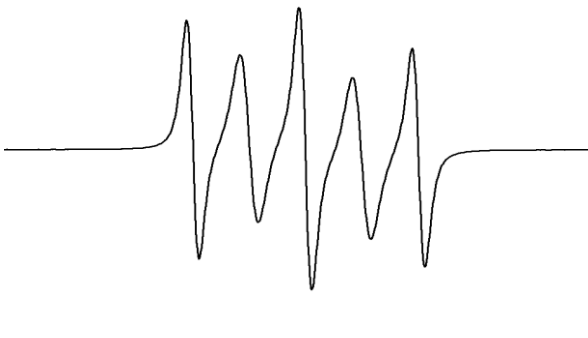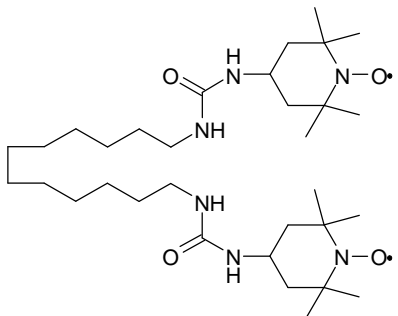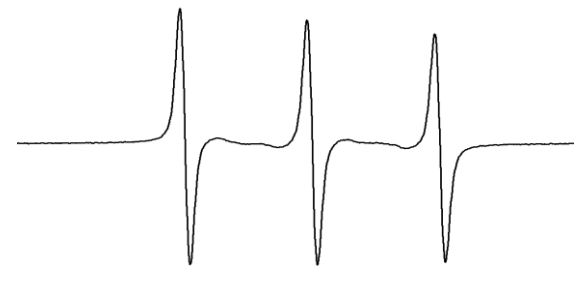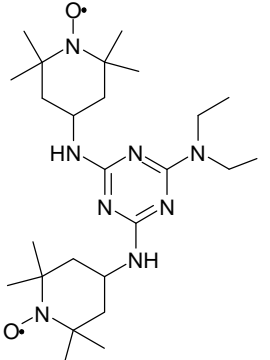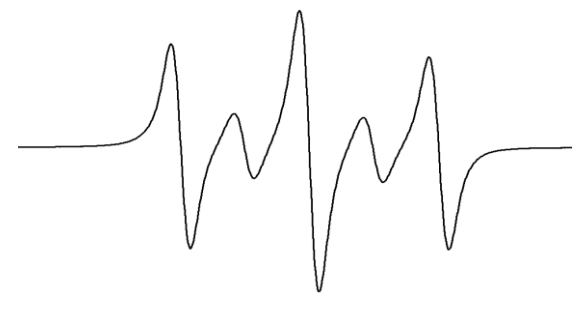
Content:

Table S1. ESR spectra in dichloromethane of the nitroxides presented in this study

1a	
1b	
1c	
1d	
1e	

2a	
2b	
2c	
2d	

Figure S1. Views of supramolecular column generated by π−π stacking interactions (a) and of the packing diagram along the crystallographic *a* axis (b) in crystal **1a**
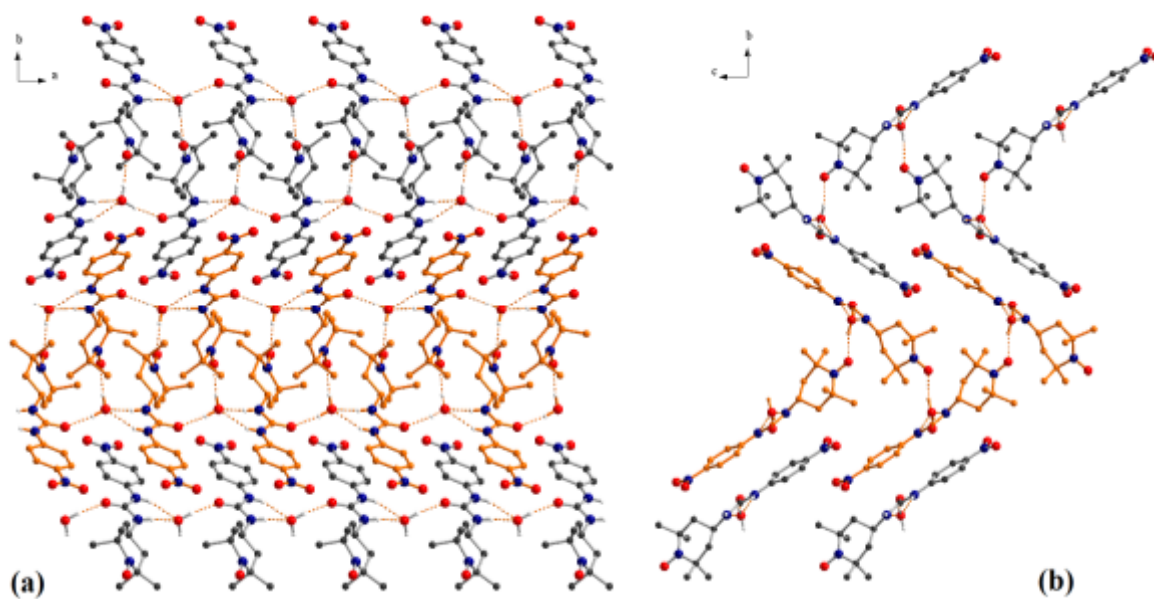
Figure S2. Views of the supramolecular architecture generated by hydrogen bonding and π−π stacking interactions along the crystallographic *c* axis (a) and *a* axis (b) in crystal **1c**
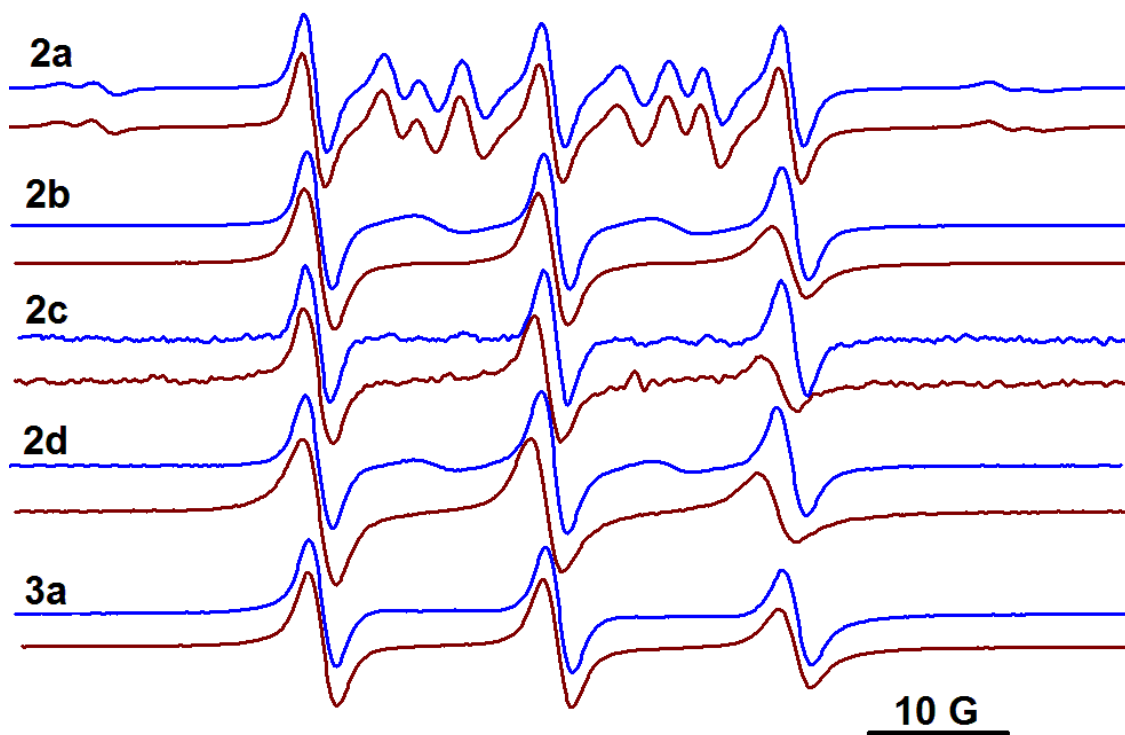
Figure S3. The ESR spectra of the radicals **2a-3a** in the absence of Q[6] - (blue spectra) and in the presence of Q[6] at highest concentration (red spectra)

Evaluation of the binding constants assuming 1:1 complexation ratio

We consider that 1:1 complexation ratio between radical and Q[6] represents the major complex component in solution, although we don't exclude the presence of complexes with higher stoechiometry (1:2 radical/Q[6]), especially at higher concentration of Q[6].

As it was mentioned in the manuscript, a_N values corresponding to radicals in aqueous solutions decrease by increasing the concentration of host concentration in most of the cases. There are two compounds, a diradical (**2a**) and the triradical which are not sensitive to the presence of Q[6]. This might be an indication that formation of complexes with higher stoechiometry is not favored.

The rotational correlation time is a parameter proportional with the molecular radius of paramagnetic entity (in our case the complex). In table S1 are presented the ratio between the values of τ_c corresponding to solution in the presence and in the absence of Q[6] (at concentration 10^{-2} M) and the ratio between the molecular weight of the complex (as sum of radical and Q[6] molecular weights). Although we are aware that might be differences between the radius ratio and molecular weight ratio we consider that this approach is still valid. It can be observed that the values of τ ratio and molecular weight ratio for a 1:1 complexation are similar. At 10^{-2} M concentration of the Q[6], the complex represents the main species, even the binding constants are relatively small.

Table S1: The ratio of τ_c values obtained for each radical in the presence of Q[6] (10^{-2} M) and in the absence of Q[6] and the ratio between molecular weight of the complex and molecular weight of the radical

Radical	1a	1b	1c	1d	1e	2b	2c	2d
τ (Q[6])/τ_c(0)	3.7	4.2	2.7	3.3	2.6	4.3	3.5	2.4
MW(complex) /MW(radical) (1:1 ratio)	3.9	3.9	3.9	3.1	3.5	3.2	2.7	3.0
MW(complex)/ MW(radical) (1:2 ratio)	6.9	6.8	6.9	5.1	6.0	5.4	4.4	5.1

A linear relationship between τ_c and the concentration of the complex in solution was assumed (eq. 1).

$$\tau_c = a[R] + b[RQ] \qquad \textbf{(1)}$$

in which [R] is concentration of the free radical, [RQ] concentration of radical/cucurbituril complex, a and b constants.

The equilibrium constant for complexation is described by the relation (2):

$$K = \frac{[RQ]}{([R_0]-[RQ])([Q_0]-[RQ])} \qquad (2)$$

$[R_0]$ represents the initial concentration of the radical and $[Q_0]$ is the initial concentration of the cucurbit[6]uril.

Concentration of the free radical in solution is described by equation 3:

$$[R] = \frac{(K[R_0]-K[b-Q_0]-1)+\sqrt{(K[R_0]-K[b-Q_0]-1)^2+4K[R_0]}}{2K} \qquad (3)$$
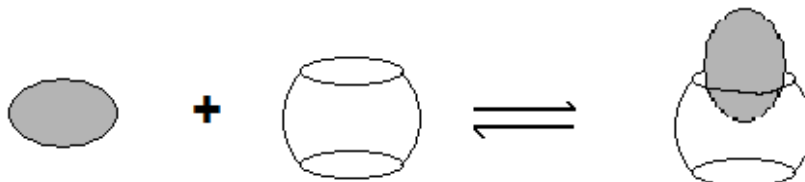
$$[RQ] = [R_0]-[R] \qquad (4)$$

Considering equations (3) and (4), the variation of τ_c as a function of K is:

$$\tau_c = a \times \frac{(K[R_0]-K[b-Q_0]-1)+\sqrt{(K[R_0]-K[b-Q_0]-1)^2+4K[R_0]}}{2K} +$$
$$b \times \left([R_0] - \frac{(K[R_0]-K[b-Q_0]-1)+\sqrt{(K[R_0]-K[b-Q_0]-1)^2+4K[R_0]}}{2K}\right) \qquad (5)$$

Determination of activation energy for the rotation motion in the complex

The complexation process schematically described here is described by variation of the enthalpy and variation of the entropy.

These parameters can be obtained from:

a) Gibbs free energy (ΔG) equation (6):

$$\Delta G = \Delta H \quad T\Delta S \qquad (6)$$

in which ΔH is enthalpy variation and ΔS is entropy variation associated in this case with the complexation process.
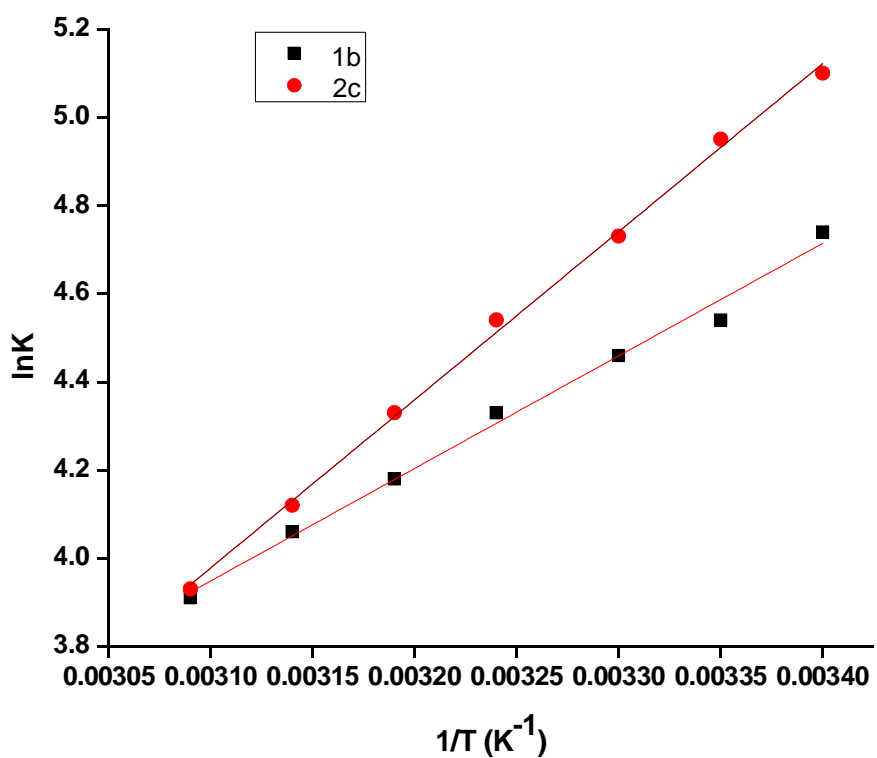
and

b) the Gibbs free energy isotherm equation (7),

$$\Delta G = -RT \ln K \qquad (7)$$

in which K represents the equilibrium constant (or binding constant).

The equations 6 and 7 are combined to obtain the van't Hoff equation:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (8)$$

ΔH and ΔS values for radicals **1b** and **2c** can be thus obtained from the slope (ΔH = -slope×R) and from the interception (ΔS = slope×R), respectively of the van't Hoff plot (Figure S4).

Figure S4. Variation of logarithmic binding constants with reciprocal temperature corresponding to Q[6]/**1b** (black) and Q[6]/**2c** complexes (red)

Radical	Slope	Interception
1b	2551.95	-3.962
2c	3813.01	-7.842