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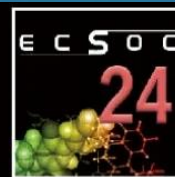
Fluorescent Calixarene Dimers: Synthesis, Optical Properties and Sensory Applications

Sérgio Costa¹, Patrícia D. Barata^{1,2,*}, Alexandra I. Costa^{1,2}, José V. Prata^{1,2}

¹Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal

²Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

*pbarata@deq.isel.ipl.pt



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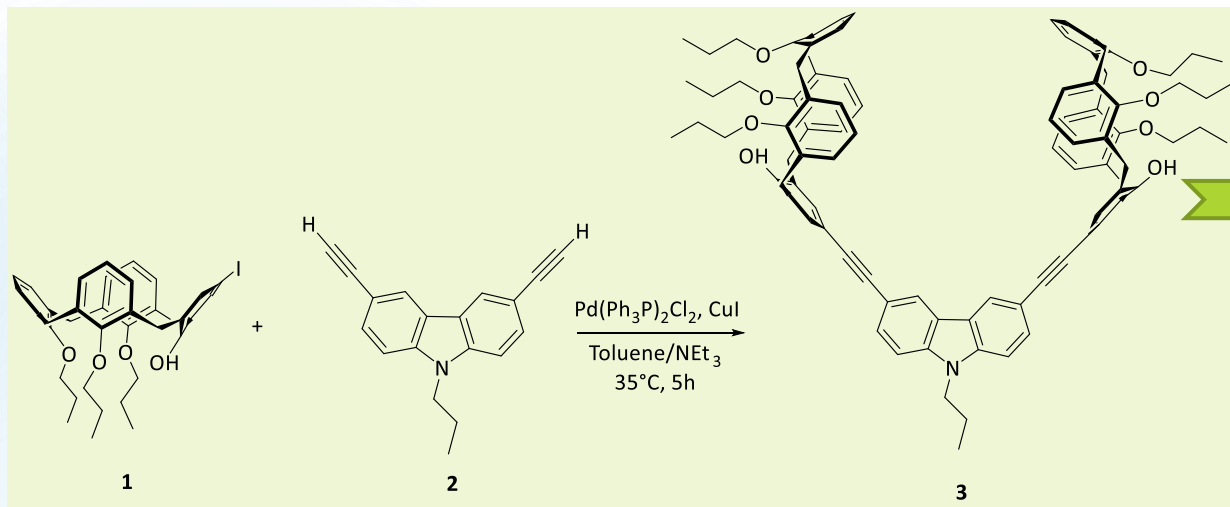
15 Nov–15 Dec 2020

Supramolecular
Chemistry

Calixarenes

Fullerenes
Detection

► Synthesis and Structural Characterization

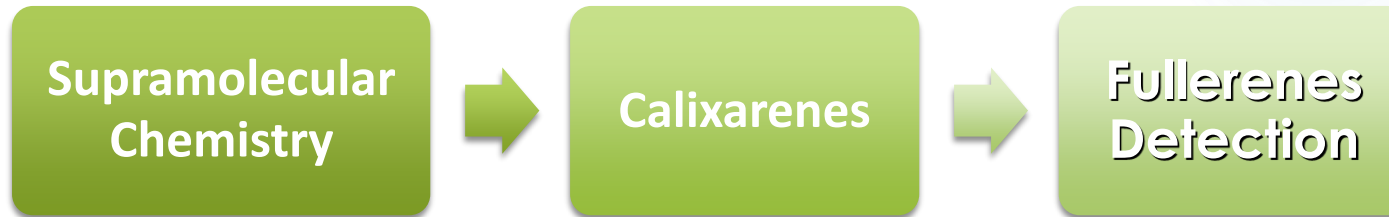


Scheme 1. Cross-coupling of calix[4]arene-triethyl-mono-iodo derivative (1) and 3,6-diethynyl-9-propyl-9H-carbazole (2).

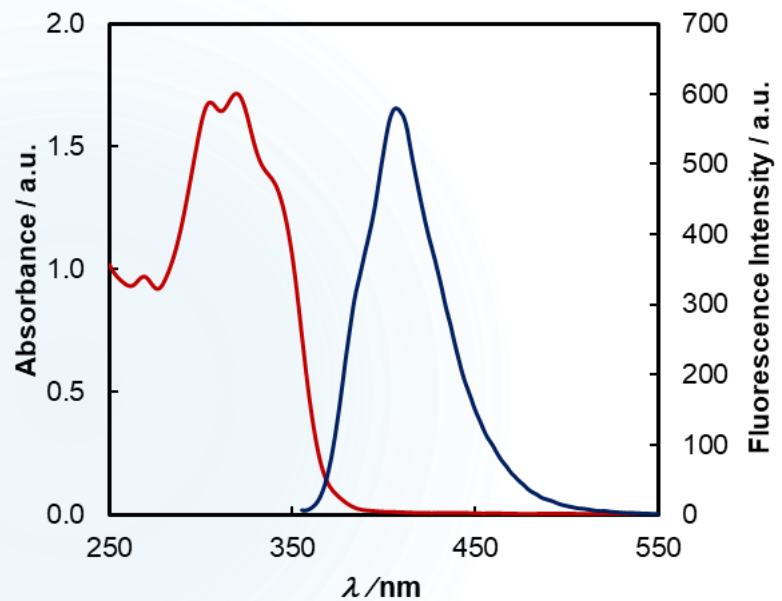
New fluorogenic bis-calix[4]arene-carbazole (3) with an enlarged intramolecular cavity able to be involved in host:guest chemistry with large organic guests.

- ✓ Sonogashira-Hagihara cross-coupling reaction
- ✓ FTIR
- ✓ ¹H/¹³C and 2D NMR

Cone conformation of the
calixarene units



► Photophysical Properties

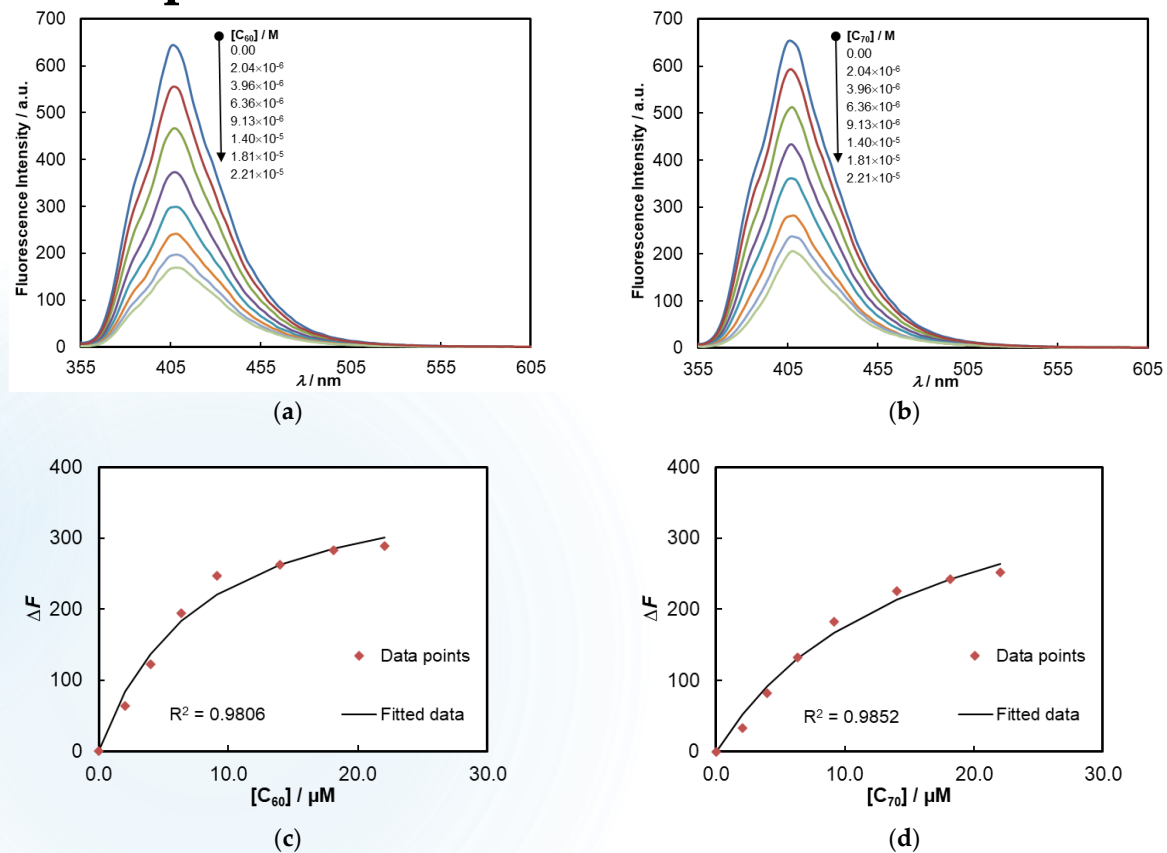


Great stability toward photobleaching in CH_2Cl_2 .

- ✓ CHCl_3 ($\Phi_F = 0.028$)
- ✓ CH_2Cl_2 ($\Phi_F = 0.13$)
- ✓ THF ($\Phi_F = 0.18$)
- ✓ Cyclohexane ($\Phi_F = 0.20$)

Figure 1. Absorption ($2.5 \times 10^{-5} \text{M}$) and fluorescence ($6.0 \times 10^{-7} \text{M}$, $\lambda_{\text{exc}} = 340 \text{ nm}$) spectra of dimer **3** in CH_2Cl_2 .

► Complexation Studies with Fullerenes



Binding affinities and free energy change



Complex	K _a / M ⁻¹	ΔG / kJ mol ⁻¹
3:C ₆₀	1.39x10 ⁵	-29.33
3:C ₇₀	6.88x10 ⁴	-27.60

Figure 2. Emission spectra of 3 (6.0x10⁻⁷ M in CH₂Cl₂) after successive additions (2.04x10⁻⁶ - 2.21x10⁻⁵ M) of fullerene C₆₀ (a) and C₇₀ (b); Curve-fitting plots for C₆₀ (c) and C₇₀ (d) derived from a non-linear regression analysis of the fluorescence data (λ_{exc} = 340 nm).

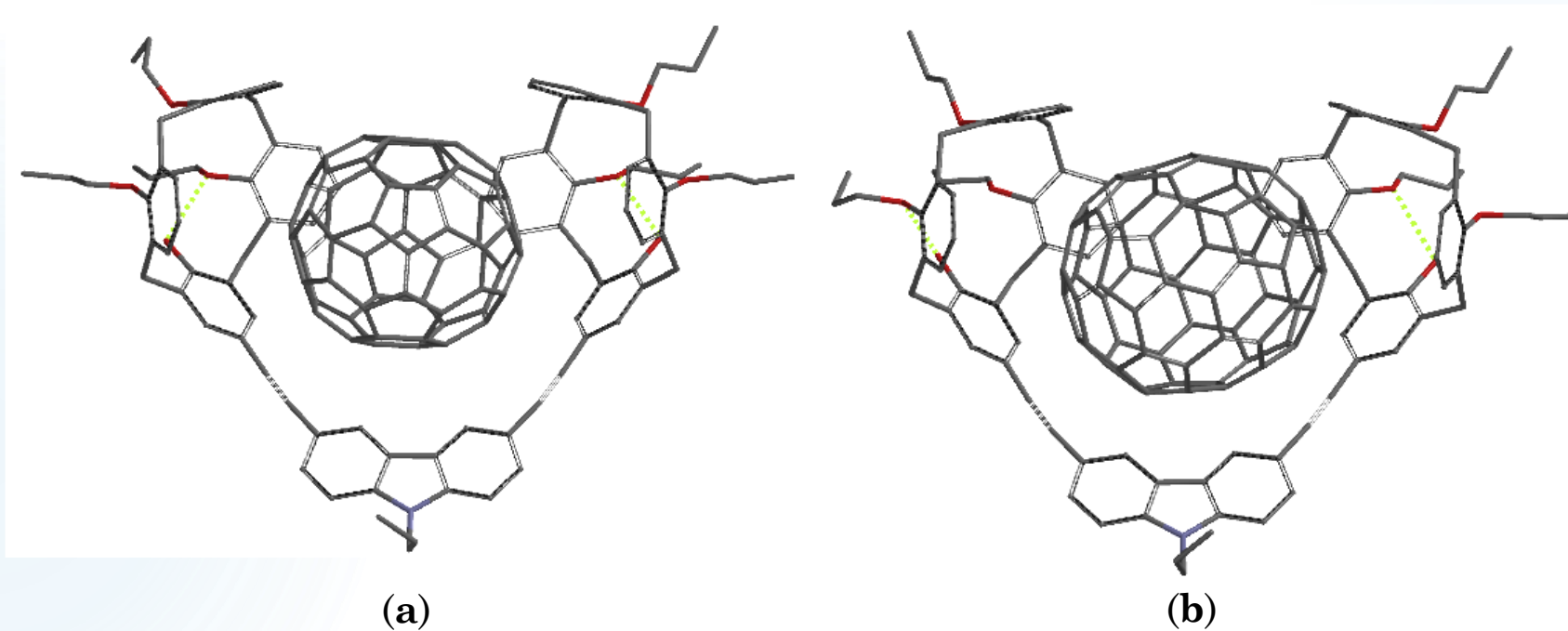


Figure 3. Best conformers of C_{60} (a) and C_{70} (b) complexes with calixarene **3**, after Monte Carlo/MMFF94 molecular mechanics calculations [Spartan'18, Wavefunction Inc., Irvine CA, USA, 2019].



► Conclusions

- New molecular receptor-based fluorescent bis-calix[4]arene-carbazole was synthesized;
- Remarkable affinity for fullerenes C_{60} and C_{70} ;
- Selectivity ratio $C_{60}/C_{70} = 2$;
- Current study \Rightarrow has been extended to other bis-calix[4]arene-carbazole conjugates, with different calixarene architectures \Rightarrow larger available space between the expected binding sites of calixarene moieties \Rightarrow new foreseen supramolecular inclusion properties towards a variety of large organic and organometallic guests.

► Acknowledgements

Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UIDB/00616/2020 and UIDP/00616/2020).