Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Di-amidosils with Tunable Structure, Morphology and Emission Quantum Yield: The Role of Hydrogen Bonding.

S. C. Nunes,[a,b*] J. Hümmer,[b] V. T. Freitas,[c] R. A. S. Ferreira,[c] L. D. Carlos,[c] P. Almeida,[a] V. de Zea Bermudez[b,d*]

[a]Chemistry Department and CICS – Health Sciences Research Centre, University of Beira Interior, 6200-001Covilhã.

[b]Chemistry Department, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real.

[c]Physics Department and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal,

[d] CQ-VR, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real.

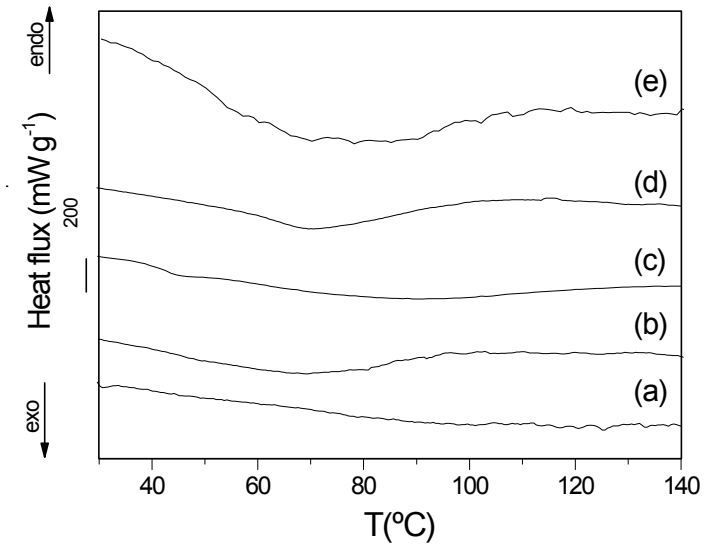

Figure S1. DSC curves of the SG-d-A(10) (a), BC-d-A(10) (b), AC-d-A(10) (600:0.2:0) (c), AC-d-A(10) (600:0.2:100(ethanol)) (d) and AC-d-A(10) (600:1:0) (e) di-amidosils.

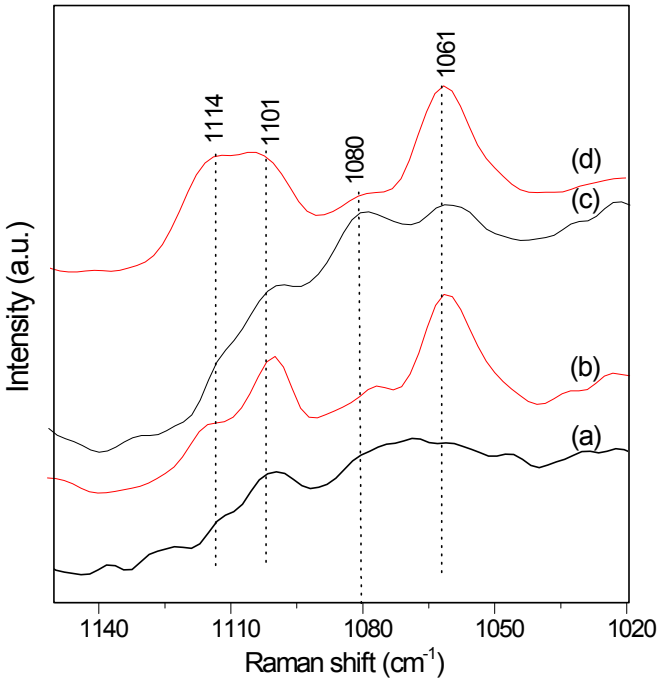

Figure S2. FT-Raman spectra of the d-A(10)-SG (a), AC-d-A(10) ((600:0.2:0) (b) AC-d-A(10) (600:0.2:100(ethanol)) (c) and AC-d-A(10) ((600:1:0) (d) di-amidosils in the νC-C region.

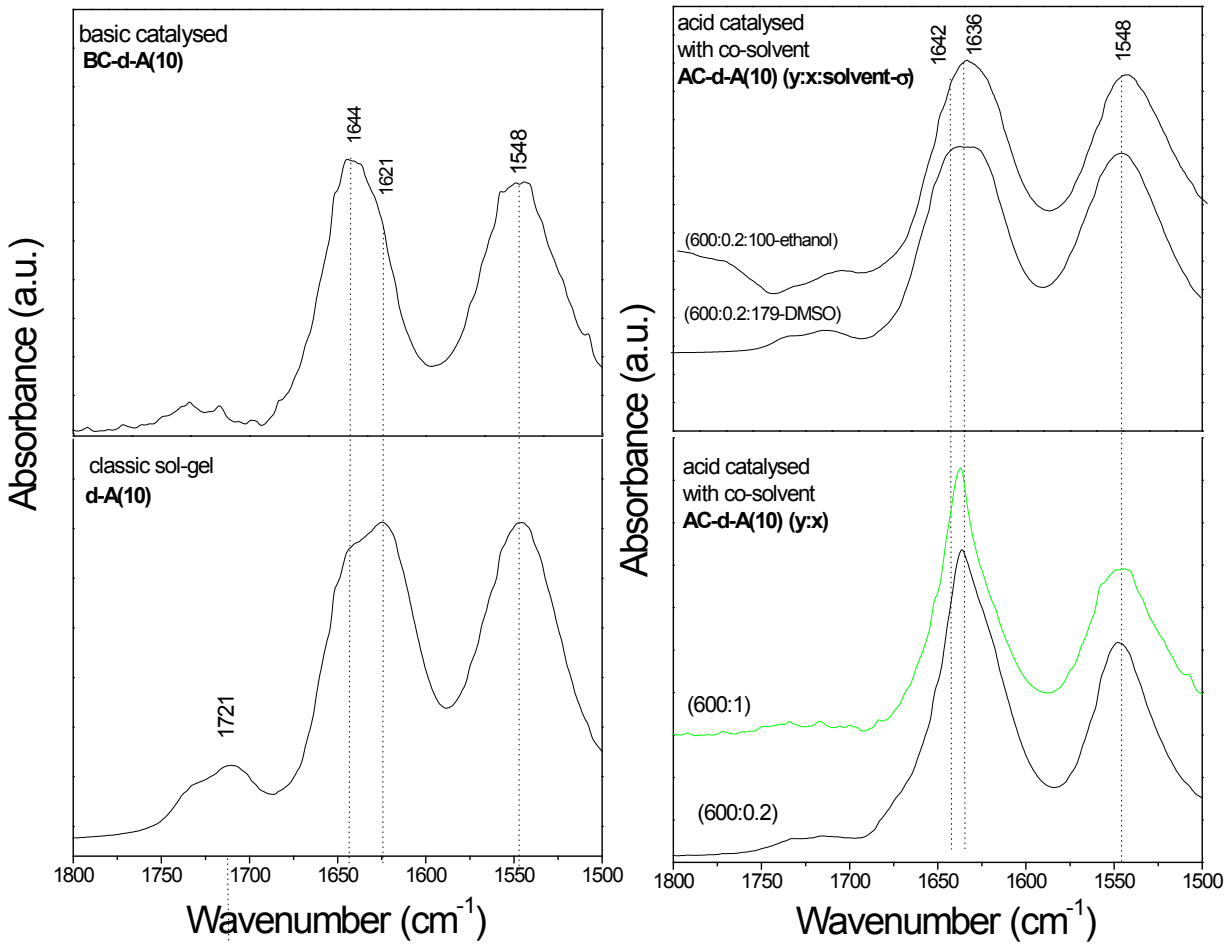

Figure S3 FT-IR spectra in the amide I and amide II regions of d-A(10), AC-d-A(10) (y:x), AC-d-A(10) (y:x: solvent-σ) and BC-d-A(10) di-amide alkyl/siloxane hybrid materials.

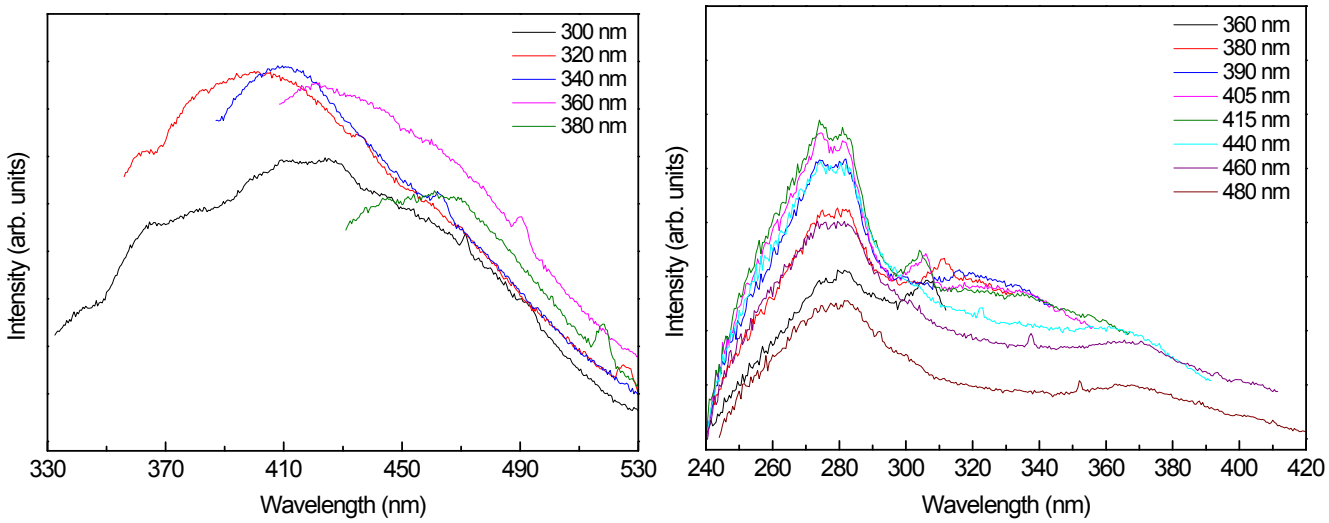

Figure S4. Low-temperature, 12 K, (left) emission and (right) excitation spectra of SG-d-A(10) as function of the excitation and monitoring wavelengths, respectively.

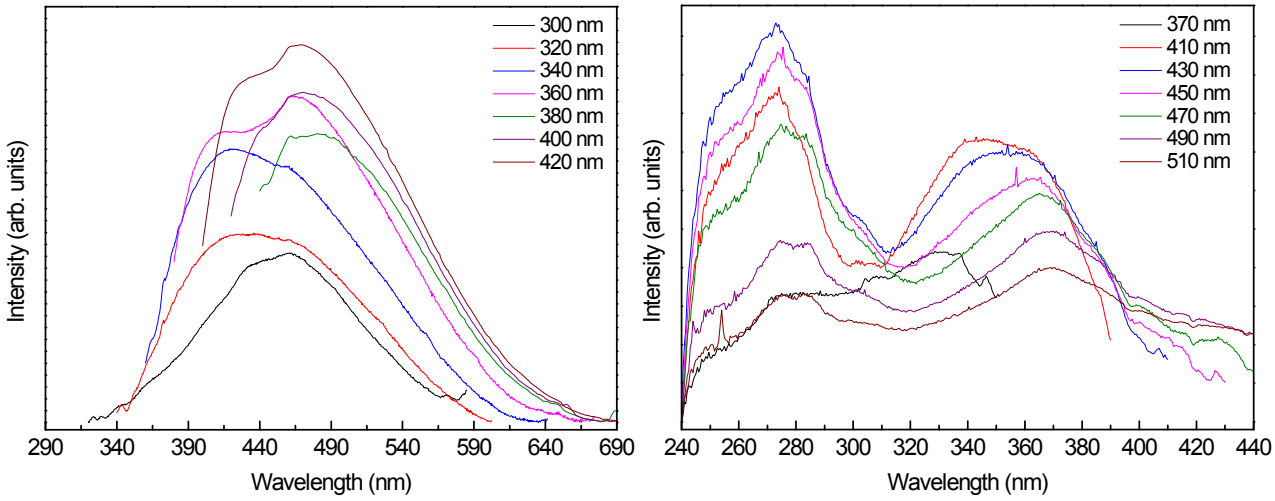

Figure S5. Low-temperature, 12 K, (left) emission and (right) excitation spectra of AC-d-A(10)(600:0.2:0) as function of the excitation and monitoring wavelengths, respectively.

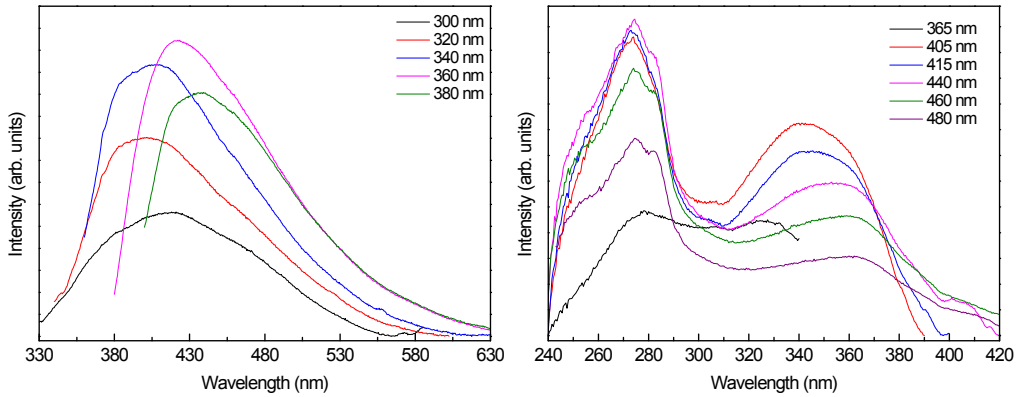

Figure S6. Low-temperature, 12 K, (left) emission and (right) excitation spectra of BC-d-A(10) as function of the excitation and monitoring wavelengths, respectively.

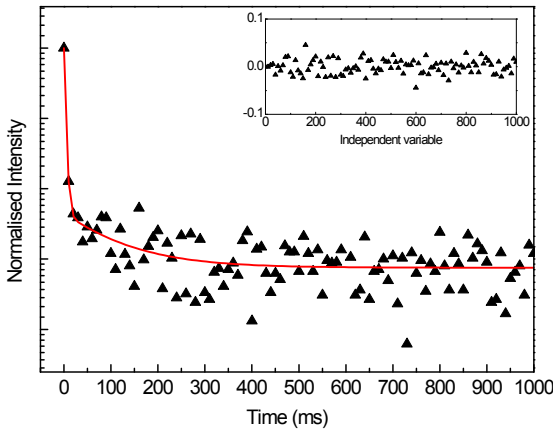

Figure S7. Low-temperature, 12 K, emission decay curves of SG-d-A(10) excited at 360 nm and monitored at 500 nm. The solid line represents the data best fit using a bi-exponential function; $I(t)=I_1\times\exp(-(t-t_0)/\tau_1+I_2\times\exp(-(t-t_0)/\tau_2)$, t_0=0.05 ms. The inset shows the regular residual plot for a better judgement of the fit quality (R_2>0.96).

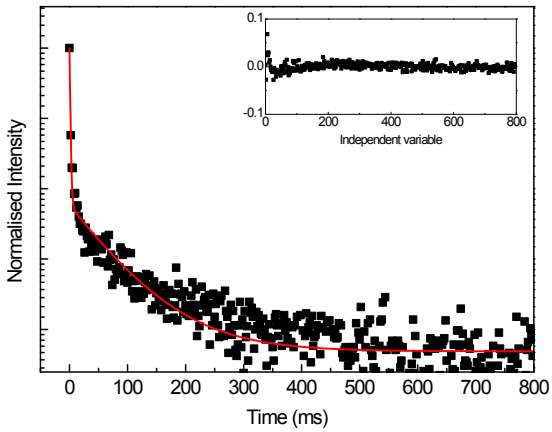

Figure S8. Low-temperature, 12 K, emission decay curves of AC-d-A(10)(600:0.2:0) excited at 360 nm and monitored at 495 nm. The solid line represents the data best fit using a bi-exponential function; $I(t)=I_1\times\exp(-(t-t_0)/\tau_1+I_2\times\exp(-(t-t_0)/\tau_2)$, t_0=0.05 ms. The inset shows the regular residual plot for a better judgement of the fit quality (R_2>0.98).

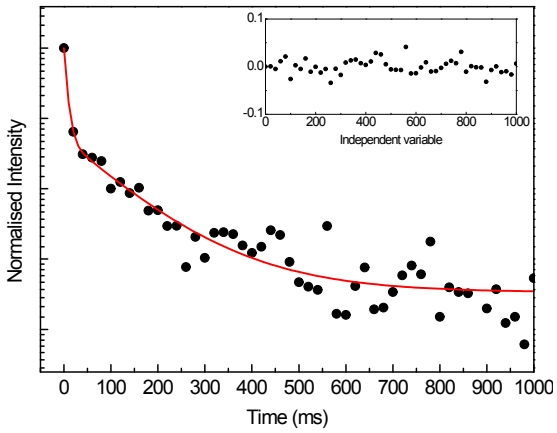

Figure S9. Low-temperature, 12 K, emission decay curves of BC-d-A(10) excited at 360 nm and monitored at 490 nm. The solid line represents the data best fit using a bi-exponential function; $I(t)=I_1\times\exp(-(t-t_0)/\tau_1+I_2\times\exp(-(t-t_0)/\tau_2)$, t_0=0.05 ms. The inset shows the regular residual plot for a better judgement of the fit quality (R_2>0.96).

Table S1 Relevant details of the various synthesis conditions used to produce the acid- and base-catalyzed d-A(10)-based di-amidosils.

Acid-catalyzed hydrolysis	AC-d-A(10) (y:x: σ(solvent))	
molar ratio precursor:H_2O:HCl:co-solvent = 1:y:x:σ		
Materials	Without co-solvent	
	1:600:1:0	1:600:0.2:0
d-ADPTES(10)	1gr (1.57 mmol)	1gr (1.57 mmol)
H_2O	17 mL (942 mmol)	17 mL (942 mmol)
HCl (1 M)	1.6 mL (1.57 mmol)	314 μL (0.314 mmol)
	With co-solvent	
	1:600:0.2:179(DMSO)	1:600:0.2:100(CH_3CH_2OH)
d-ADPTES(10)	1g (1.57 mmol)	1g (1.57 mmol)
H2O	17 mL (942 mmol)	17 mL (942 mmol)
HCl (1 M)	314 μL (0.314 mmol)	314 μL (0.314 mmol)
DMSO	20 mL (0.281 mol)	-
CH_3CH_2OH	-	9 mL (0.157 mol)
Base-catalyzed hydrolysis	BC-d-A(10)	
	molar precursor:H_2O:CH_3CH_2OH:NaOH = 1:39:315:0.23	
d-ADPTES(10)	0.8421 g (1.32 mmol)	
CH_3CH_2OH	3 mL (51.4 mmol)	
H_2O	7.5 mL (417 mmol)	
NaOH (3 M)	100 μL (0.3 mmol)	

Table S2 Details and attribution of the components of the FT-IR amide I and amide II bands of the SG-d-A(10), AC-d-A(10)-based and BC-d-A(10) di-amidosils. F, D and O stand for free, disordered and ordered.

FT-IR amide I and amide II bands								
Samples		$\bar{\nu}$ (in cm^{-1}) (fwhm in cm^{-1}) (area in %)						
SG-d-A(10)		1733 (18) (3)	1710 (28) (3.4)	1656 (22) (5.4)	1639 (28) (22)	1617 (31) (23)	1562 (35) (19)	1537 (35) (23)
AC-d-A(10) (y:x)	y = 600; x = 1			1647 (16) (15)	1635 (16) (25)	1619 (23) (15)	1557 (24) (17)	1543 (31) (25)
	y = 600; x = 0.2			1649 (25) (13)	1635 (18) (22)	1619 (22) (29)	1555 (24) (14)	1543 (30) (21)
AC-d-A(10) (y:x:σ-solvent)	y = 600; x = 0.2, 179 -DMSO	1726 (16) (1.0)	1707 (21) (2.6)	1650 (25) (12)	1636 (33) (20)	1618 (35) (21)	1558 (40) (21)	1539 (41) (22)
	y = 600; x = 0.2:100- ethanol	1730 (13) (0.5)	1713 (14) (0.7)	1652 (24) (11	1636 (29) (22)	1618 (29) (18)	1560 (37) (19)	1540 (39) (27)
BC-d-A(10)		1736 (26) (23)	1718 (27) (1.4)	1656 (25) (17)	1640 (19) (16)	1623 (25) (19)	1560 (26) (20)	1539 (27) (24)
Attribution		F	D1	D2	O1	O2	amide II	
		amide I						