

High Resolution Mass Spectrometry (HRMS)

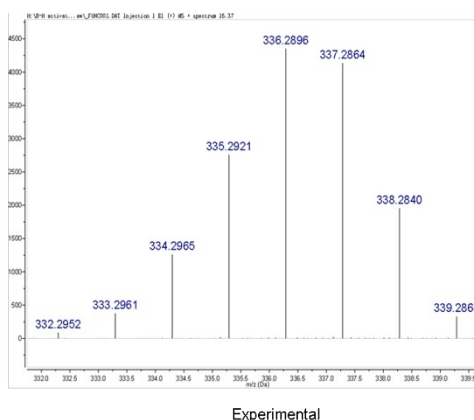
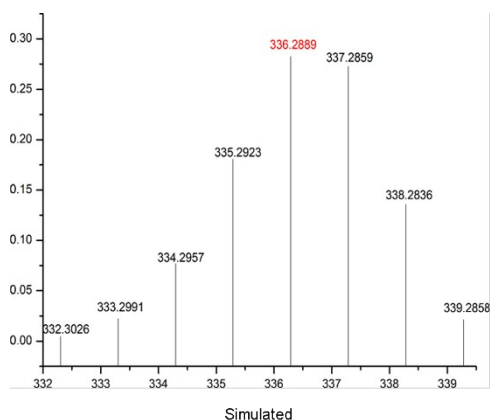


Figure S1. HRMS of mFI-Cb-H.

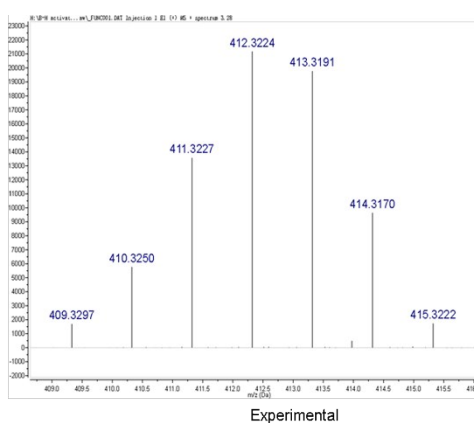
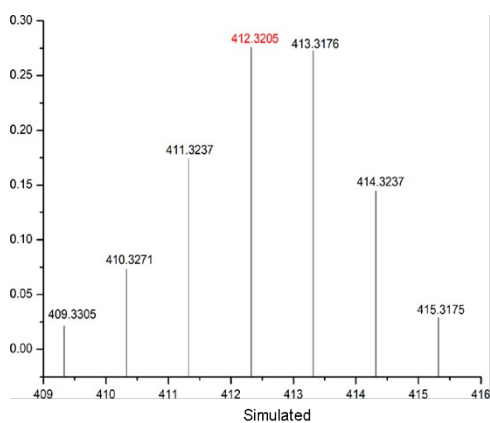


Figure S2. HRMS of mFI-Cb-Ph.

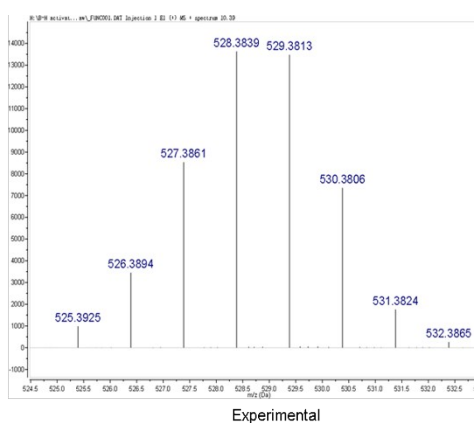
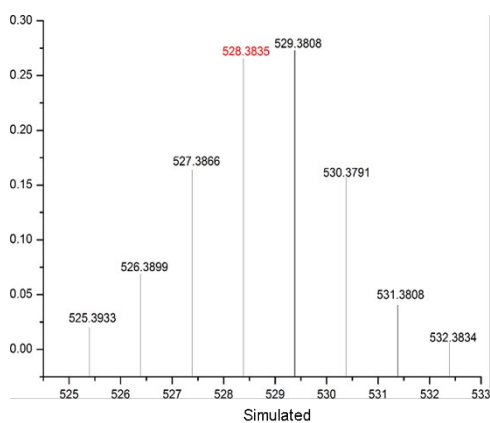


Figure S3. HRMS of DmFI-Cb.

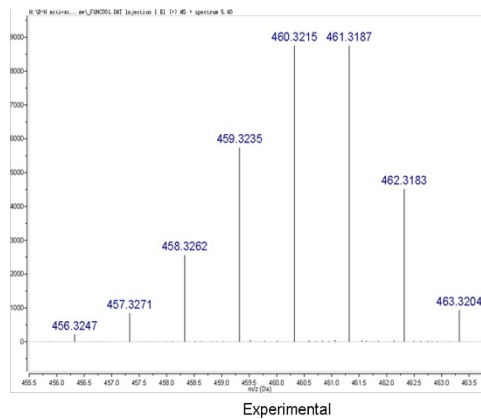
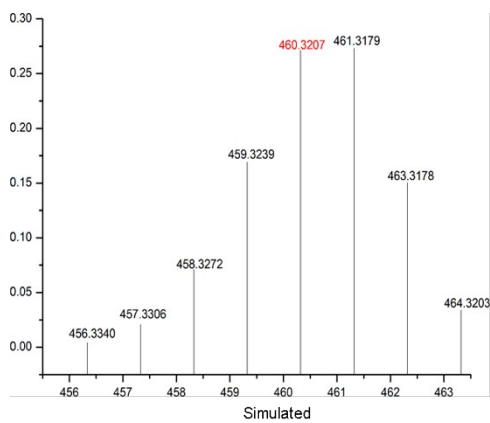


Figure S4. HRMS of pFI-Cb-H.

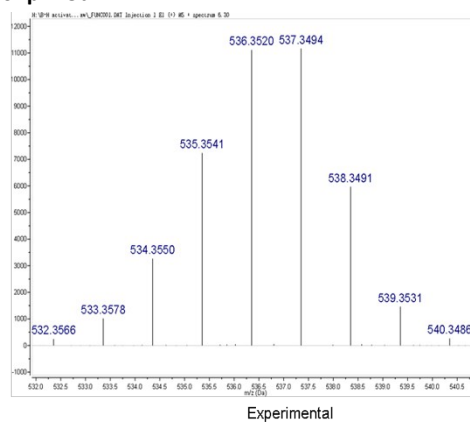
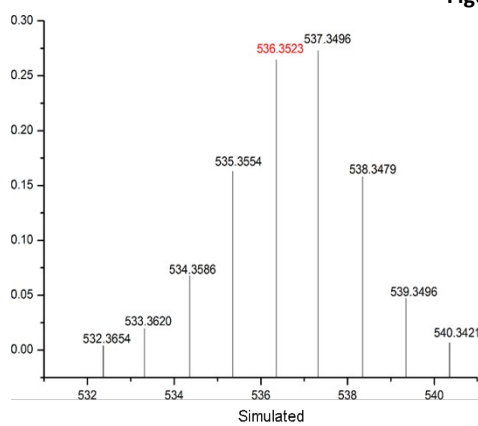


Figure S5. HRMS of pFI-Cb-Ph.

Table S1. Structural refinement data of crystals

	mFI-Cb-Ph*	DmFI-Cb&	pFI-Cb-H#
CCDC number	1527646	1527647	1536124
Formula	C ₂₃ H ₂₈ B ₁₀	C ₃₂ H ₃₆ B ₁₀	C ₂₇ H ₂₈ B ₁₀
Crystal system	triclinic	triclinic	tetragonal
Space group	P -1	P -1	I41/a
a, Å	10.2378(4)	10.7377(4)	29.1255(9)
b, Å	10.7582(5)	15.4048(6)	29.1255(9)
c, Å	11.6502(6)	18.3711(7)	14.6448(5)
α(°)	90.007(2)	90.481(2)	90.00
β(°)	102.099(2)	97.830(2)	90.00
γ(°)	110.257(2)	91.483(2)	90.00
V, Å ³	1173.35(9)	3009.3(2)	12423.1(7)
ρ/g.cm ⁻³	1.168	1.167	0.985
Z	2	4	16
μ (mm ⁻¹)	0.059	0.061	0.051
F(000)	432.0	1112.0	3839
R1(reflections)	0.0668	0.0489	0.0890
wR2(reflections)	0.1491	0.1145	0.3329
)			
GOOF	0.939	0.994	0.826

* Crystals of **mFI-Cb-Ph** were grown from slow evaporation of ethanol solution

& Crystals of **DmFI-Cb** were grown from a hot methanol/ethanol (1:1) solution

Crystals of **pFI-Cb-H** were grown from a saturated chloroform solution. Disordered lattice solvent molecules could not be modelled (even at 120K) and were therefore removed from the refinement using PLATON SQUEEZE¹. The molecular structure of **pFI-Cb-H** was confirmed despite the poor diffraction data.

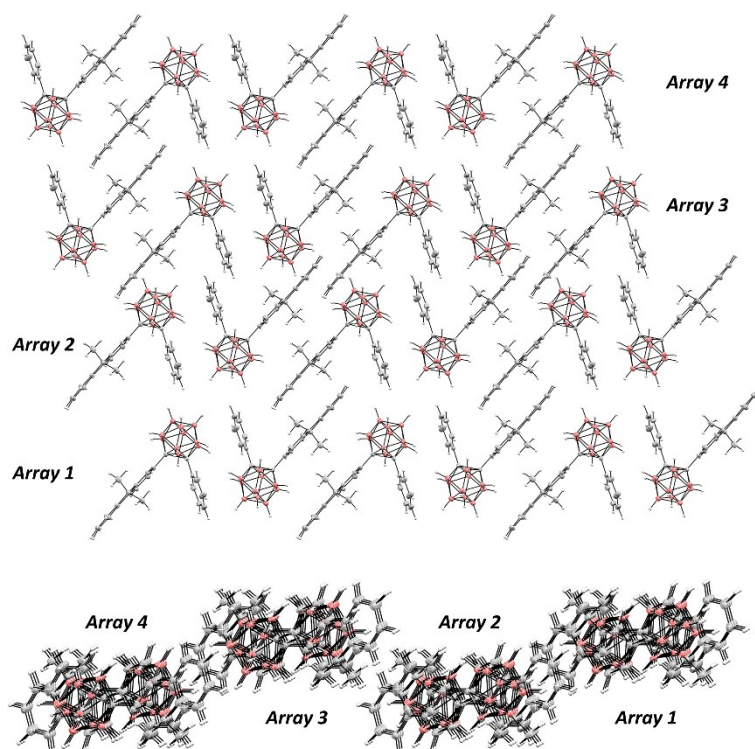


Figure S6. Crystal packing of mFI-Cb-Ph.

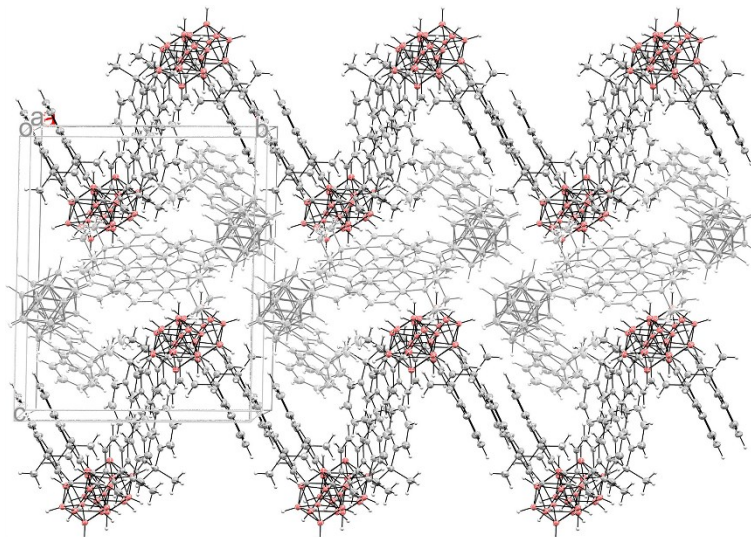


Figure S7. Crystal packing of DmFI-Cb including both *cis*- and *trans*- (gray) conformers.

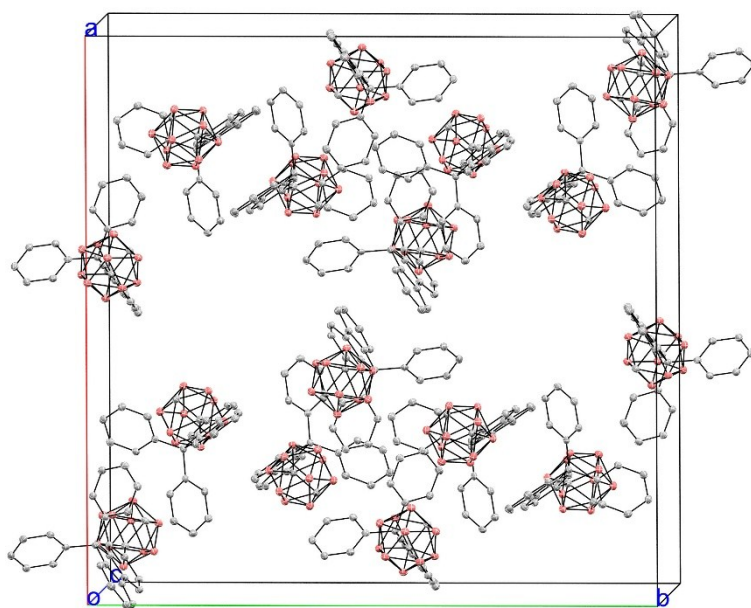


Figure S8. Unit cell of pFI-Cb-H. Hydrogens have been omitted for clarity.

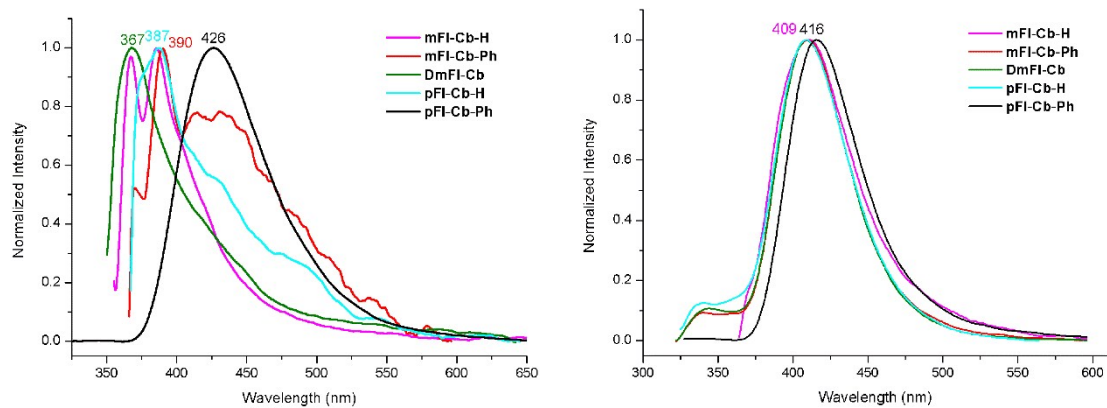


Figure S9. Emission spectra (excitation at 300 nm) of FI-Cb analogues in CH_2Cl_2 (left) and CH_3CN (right). The quantum efficiency is around 0.1%.

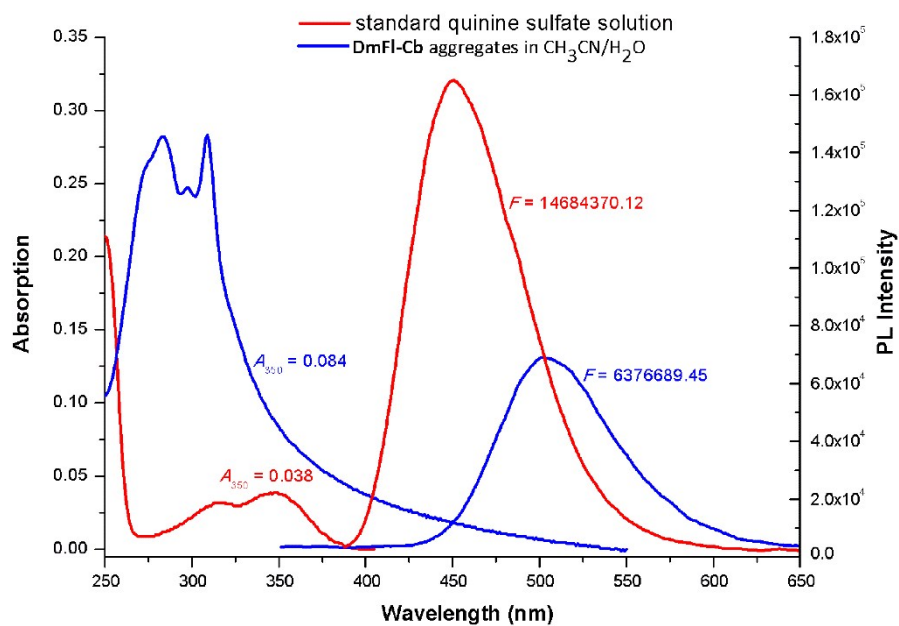


Figure S10. Absorption and emission spectra (excitation at 350 nm) of quinine sulfate solution and DmFI-Cb aggregates (10^{-5} mol/L) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4:6) solution. The quantum yield was estimated using quinine sulfate as a standard ($\Phi = 0.55$).

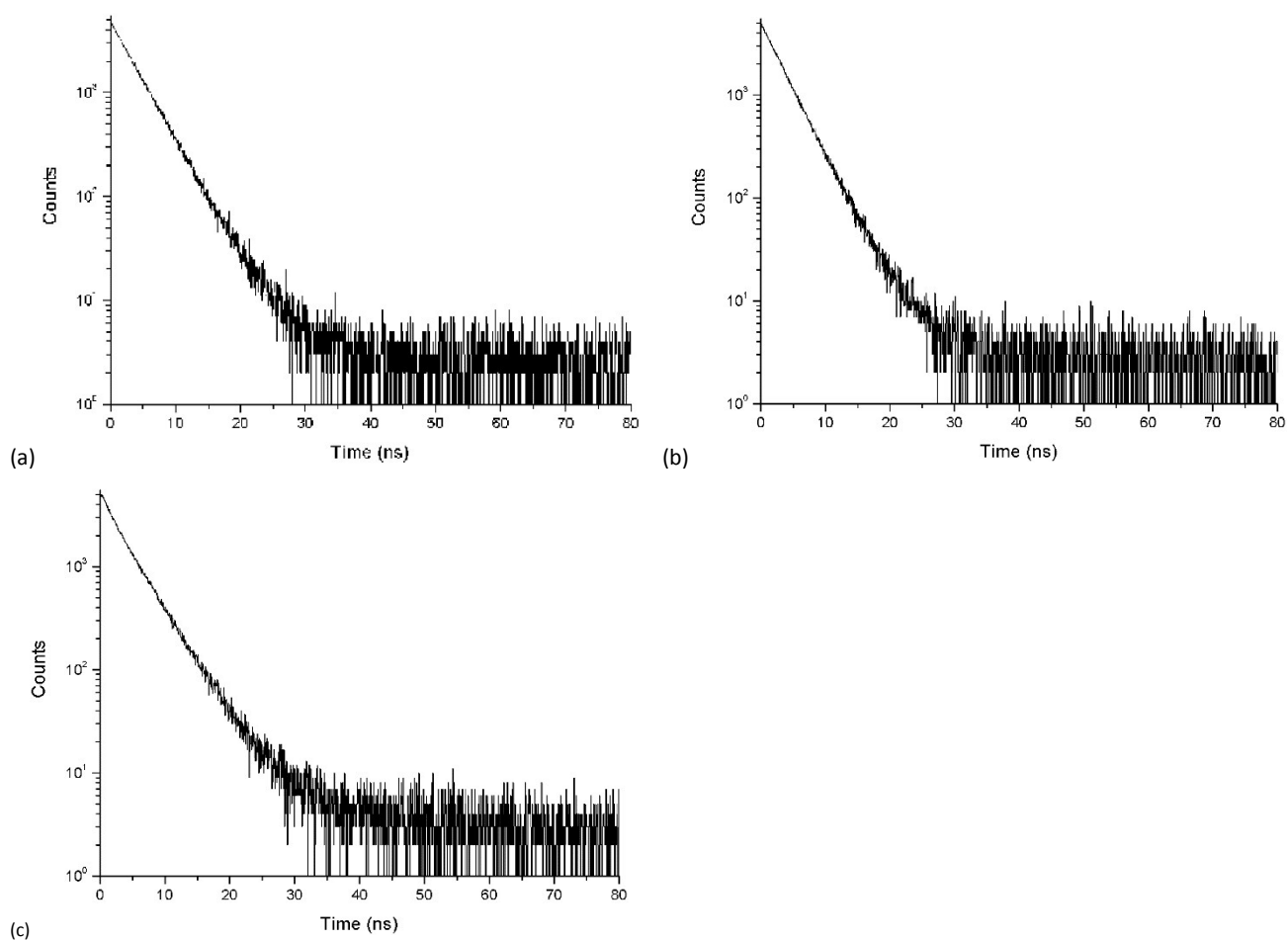


Figure S11. PL decay of the solid FI-Cb analogues, mFI-Cb-Ph (a), DmFI-Cb (b) and pFI-Cb-Ph (c).

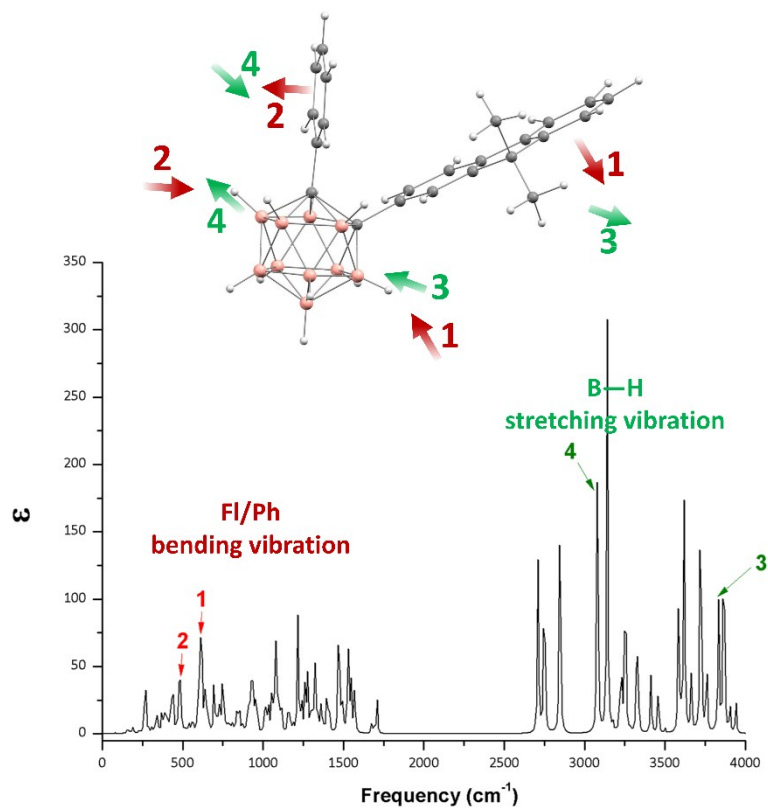


Figure S12. Simulated infrared spectrum of **mFI-Cb-Ph**. Selected vibrations relative to the aggregation are shown in colored arrows.

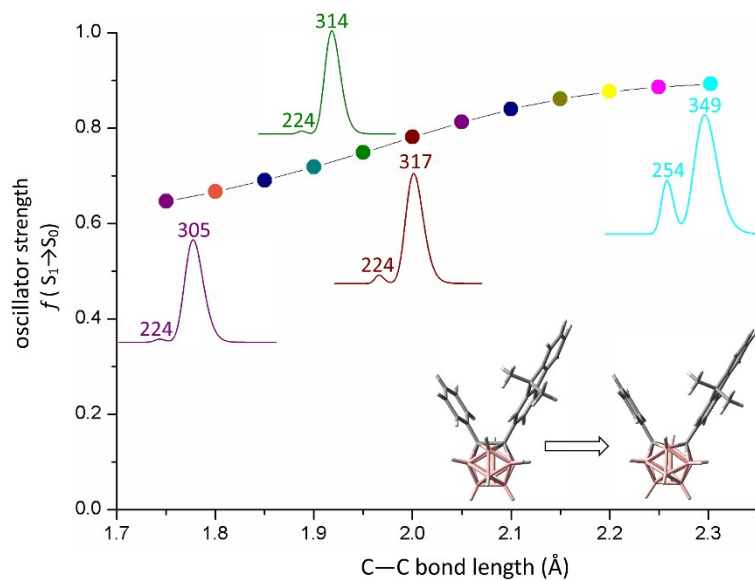


Figure S13. Calculated oscillator strengths (f) of electronic transitions from different excited states (S_1) to the ground state (S_0) of the **mFI-Cb-Ph** monomer. Excited-state structures were obtained by TD-DFT optimization varying the cage C—C bond lengths from 1.75 Å to 2.30 Å.

Table S2. Calculated electronic transitions of **mFI-Cb-Ph** from the ground state to the lowest five excited states for different aggregations.

mFI-Cb-Ph monomer		
λ_{calc} (nm)	f	Assignment (> 5%)
261.95	0.6030	H → L (91.7%)
245.25	0.0582	H-2 → L (31.6%); H → L (5.6%); H → L+2 (41.9%); H → L+3 (11.3%)
239.97	0.0193	H-1 → L (47.9%); H-1 → L+1 (6.2%); H-1 → L+6 (5.8%); H → L+3 (10.5%); H → L+5 (24.1%)
227.08	0.0032	
207.03	0.1055	H-3 → L (19.0%); H-3 → L+1 (31.8%); H-2 → L (9.0%); H → L+1 (21.6%)
mFI-Cb-Ph dimer-FI		
λ_{calc} (nm)	f	Assignment (> 5%)
266.88	0.0000	

261.52	1.0051	H-1 → L (47.7%); H → L+1 (46.3%)
246.04	0.0000	
245.68	0.1030	H-5 → L (14.7%); H-4 → L+1 (14.7%); H-1 → L+4 (20%); H-1 → L+7 (7%); H → L+5 (19%); H → L+6 (19%)
240.85	0.0000	
mFl-Cb-Ph dimer-Ph		
λ_{calc} (nm)	f	Assignment (> 5%)
262.63	1.3438	H-1 → L (47.9%); H → L+1 (49.4%)
261.30	0.0001	
245.26	0.1224	H-9 → L+1 (6.9%); H-8 → L (7.2%); H-6 → L+1 (11.6%); H-5 → L (10.2%); H-1 → L+4 (25%); H → L+5 (24.6 %)
245.14	0.0000	
239.91	0.0002	
mFl-Cb-Ph trimer		
λ_{calc} (nm)	f	Assignment (> 5%)
266.83	0.0081	
262.35	1.6397	H-2 → L (65.8%); H-1 → L+1 (20.4%); H → L+2 (13.7%)
261.09	0.1306	H-2 → L (35.1%); H-1 → L+1 (29.8%); H → L+2 (35.2%)
245.98	0.0001	
245.62	0.1169	H-8 → L+1 (13.2%); H-6 → L+2 (15.4%); H-1 → L+6 (20.5%); H-1 → L+9 (7.1%); H → L+8 (27.9%)
mFl-Cb-Ph tetramer		
λ_{calc} (nm)	f	Assignment (> 5%)
266.97	0.0156	H-3 → L (16.1%); H-3 → L+1 (5.9%); H-2 → L (5.9%); H-2 → L+1 (16.2%); H-1 → L+2 (27.5%); H → L+3 (28.4%)
266.66	0.0000	
262.05	2.2075	H-3 → L (20.2%); H-3 → L+1 (7.4%); H-2 → L (7.4%); H-2 → L+1 (20.2%); H-1 → L+2 (22%); H → L+3 (22.8%)
260.96	0.0000	
245.97	0.0001	

Table S3. Calculated electronic transitions of **cis-DmFl-Cb** tetramer from the ground state to the lowest five excited states.

λ_{calc} (nm)	f	Assignment (> 4%)
271.86	0.7101	H-7 → L (12.2%); H-6 → L+1 (7%); H-6 → L+3 (4.2%); H-5 → L (17.9%); H-5 → L+2 (5.7%); H-5 → L+4 (10.2%); H-4 → L+1 (5.2%); H-4 → L+3 (6.5%); H-4 → L+5 (11%); H-4 → L+7 (4.4%); H-1 → L (4.4%); H-1 → L+4 (4.8%); H → L+1 (6.6%)
269.53	0.0000	
269.39	0.7311	H-7 → L+2 (6.6%); H-6 → L+3 (4.9%); H-3 → L+2 (10.4%); H-3 → L+6 (8.2%); H-2 → L+3 (8.5%); H-2 → L+5 (5.4%); H-2 → L+7 (5.2%); H-1 → L+2 (7.4%); H-1 → L+6 (6.6%); H → L+1 (6.7%); H → L+7 (4.8%)

268.25 0.0000

262.65 0.0000

Table S4. Selected energy levels of **mFI-Cb-Ph** for different aggregations.

	<i>monomer</i>	<i>dimer-Fl</i>	<i>dimer-Ph</i>	<i>trimer</i>	<i>tetramer</i>
L+3	1.483	0.973	1.091	0.979	0.467
L+2	1.161	0.954	1.003	0.463	0.452
L+1	0.910	0.396	0.390	0.410	0.410
L	0.309	0.387	0.378	0.380	0.410
H	-8.030	-7.897	-7.960	-7.839	-7.842
H-1	-8.863	-7.903	-7.965	-7.883	-7.846
H-2	-9.089	-8.693	-8.800	-7.968	-7.882
H-3	-9.204	-8.709	-8.801	-8.645	-7.882

Table S5. Selected energy levels of **cis-DmFI-Cb** for different aggregations.

	<i>monomer</i>	<i>dimer</i>	<i>tetramer</i>
L+7	2.137454	1.328732	0.421232
L+6	1.989696	1.31431	0.412797
L+5	1.918947	1.237029	0.376333
L+4	1.901803	1.230499	0.32953
L+3	1.437305	0.444906	0.200276
L+2	1.339344	0.399463	0.174697
L+1	0.521642	0.222317	0.115648
L	0.288713	0.143132	0.071566
H	-7.89076	-7.94219	-7.97538
H-1	-7.94572	-8.00613	-7.97538
H-2	-8.8007	-8.0113	-8.023
H-3	-8.84098	-8.08722	-8.023
H-4	-9.0701	-8.86465	-8.05049
H-5	-9.11908	-8.92778	-8.08341
H-6	-9.7746	-8.93241	-8.12287
H-7	-9.86494	-8.93268	-8.12314

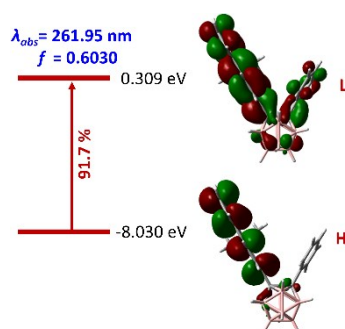


Figure S13. Electronic transition of the **Ph-Cb-mFI** monomer corresponding to the lowest energy absorption.

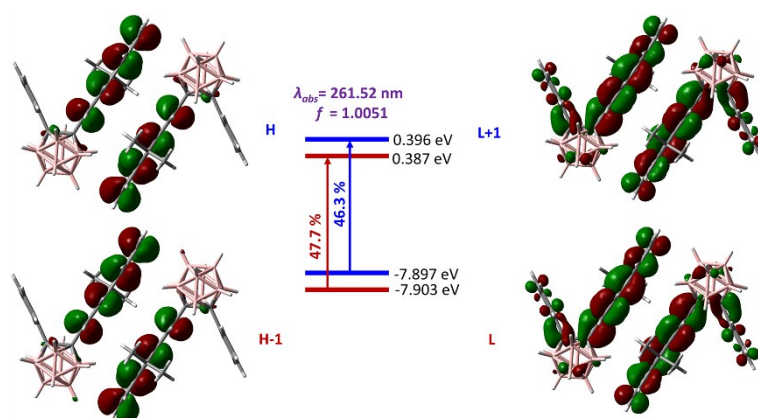


Figure S14. Electronic transition of the FI-stacked dimer **Ph-Cb-mFI** corresponding to the lowest energy absorption.

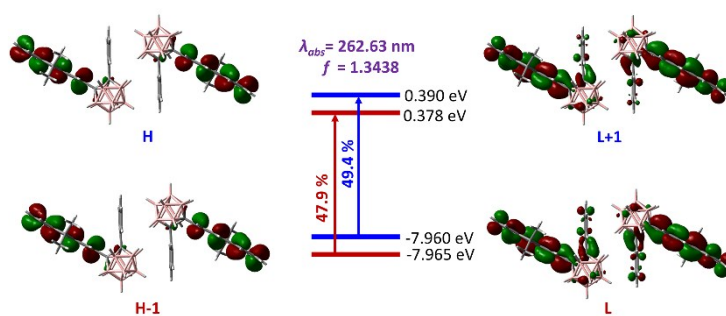


Figure S15. Electronic transition of the Ph-stacked dimer **Ph-Cb-mFI** corresponding to the lowest energy absorption.

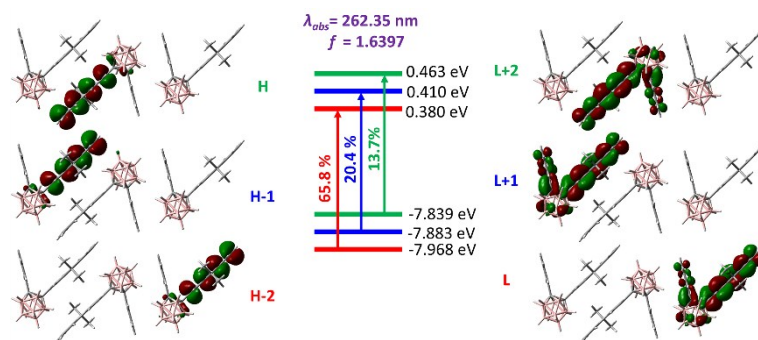


Figure S16. Electronic transition of the **Ph-Cb-mFI** trimer corresponding to the lowest energy absorption.

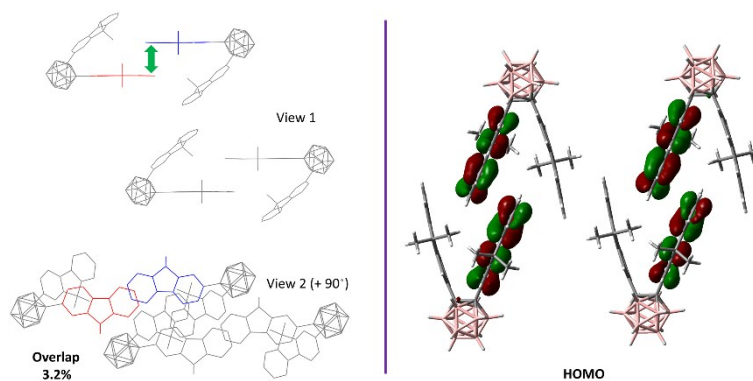


Figure S17. (left) Views of *cis*-DmFI-Cb illustrating the π -overlap. View 2 is rotated 90° compared with view 1. The overlap ratio (3.2%) was calculated with Adobe Photoshop 2017 v.18.0.1 using the integrals of overlap and FI. (right) HOMO of *cis*-DmFI-Cb.

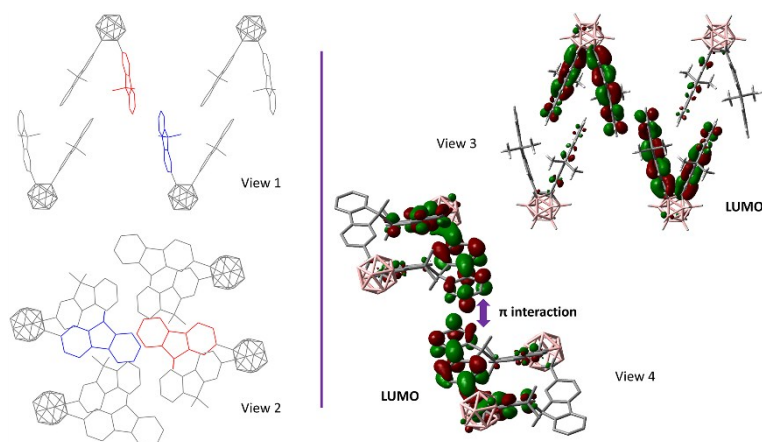


Figure S18. (left) Views of *cis*-DmFI-Cb emphasizing the other adjacent pair of FI moieties; no overlap is observed. (right) LUMO of *cis*-DmFI-Cb.

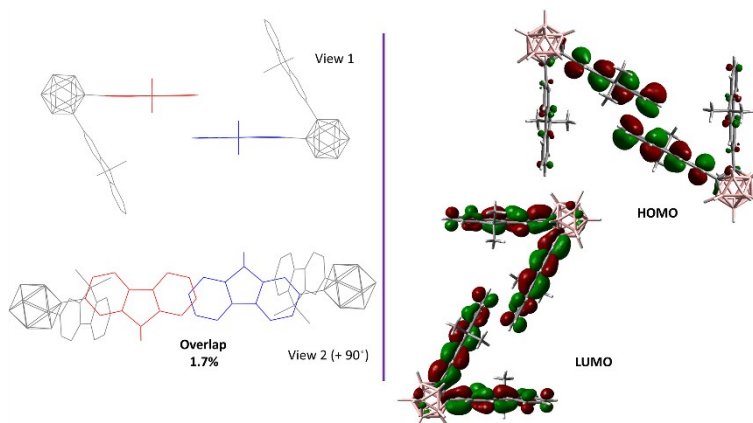


Figure S19. (left) Views of *trans*-DmFI-Cb illustrating adjacent FI moieties. View 2 is rotated 90° compared with view 1. The overlap ratio (1.7%) was calculated with Adobe Photoshop 2017 v.18.0.1 using the integrals of overlap and FI. (right) HOMO and LUMO of *trans*-DmFI-Cb.

Reference

1. A.L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 9.