Entwined Dimers Formation from Self-Complementary bis-Acrdiniums

H.-P. Jacquot de Rouville,*a,b Nathalie Zorn, c Emmanuelle Leize-Wagner, c V. Heitz*a

aUniv Paris Diderot, Sorbonne Paris Cite, ITODYS, UMR CNRS 7086, 15 rue J-A de Baif, 75013 Paris, France
E-mail : h-p.jacquot@univ-paris-diderot.fr
bLaboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels, Institut de Chimie de Strasbourg, CNRS/UMR 7177, 4, rue Blaise Pascal, 67000 Strasbourg, France
E-mail : v.heitz@unistra.fr
E-mail : hpjacquot@unistra.fr
cLaboratoire de Spectrométrie de Masse des Interactions et des Systèmes (LSMIS), UMR 7140 (Unistra-CNRS), Université de Strasbourg, France

Supporting Information

Table of Contents

1. Material and Methods................................................................. S1
2. Synthesis.................................................................................. S2
3. Structural Characterizations of the Synthesized Compounds.......... S6
   Characterizations of 2·PF6 (1H, 13C NMR and ESI-MS)................. S6
   Characterizations of 3 (1H, 13C NMR and ESI-MS)..................... S8
   Characterizations of 4 (1H, 13C NMR and ESI-MS)..................... S10
   Characterizations of 5 (1H, 13C NMR and ESI-MS)..................... S12
   Characterizations of the equilibrium between 12+ and (1·)–+........ S14
   Characterizations of the ion pair in (1)2·4PF6................................ S29
4. UV-Vis Characterization of 1·2PF6............................................ S31
5. Crystallographic Data of (1)2·4PF6.......................................... S32
6. References............................................................................. S33
1. Material and General Methods.

Synthesis. All chemicals were of the best commercially available grade and used without further purification. 10-Methyl-9(10H)-acridone was synthesized according to previously reported procedure. All compounds were synthesized using schlenk technics and were fully characterized by 1D ($^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H} and $^{19}$F{$^1$H}) and 2D (COSY, HSQC and HMBC) NMR experiments and by mass spectrometry experiments. THF was dried using drystation GT S100 or distilled over sodium/benzophenone before use. Anhydrous DMF was purchased from ACROS organics. Column chromatography was carried out using silica gel (Merck, silica gel 60, 63−200 or 40−63 μm). Mass spectra were obtained by using a Bruker MicroTOF spectrometer in electrospray mode (ESI). Nuclear magnetic resonance (NMR) spectra for $^1$H were acquired on a Bruker AVANCE 300, 400, 500 and 600 spectrometers. $^{13}$C spectra were acquired on a Bruker AVANCE 500 spectrometer. $^{19}$F spectra were acquired on a Bruker AVANCE 300 spectrometer. The $^1$H and $^{13}$C spectra were referenced to residual solvent peaks. Measures of self-diffusion coefficients were performed on a Bruker 600 MHz spectrometer-Avance III, equipped with a BBI probe (Bruker BBI probe, developing a pulse field gradient of 5 G/cm/Å). The sample was thermostated at 298 K unless otherwise stipulated. Diffusion NMR data were acquired using a Stimulated Echo pulse sequence with bipolar z gradients. Limited Eddy current delay was fixed to 5 ms. The diffusion time and the duration of the gradients were optimized for each sample. A recycling delay of at least 5 s was respected between scans. DOSY spectra were generated by the DOSY module of the software Topspin to build the diffusion dimension. The diffusion coefficients were compared to CH$_3$CN or H$_2$O as an internal standards ($\eta$(CD$_3$CN) = 3.57 × 10$^{-4}$ Pa.s and $\eta$(D$_2$O) = 1.13 × 10$^{-3}$ Pa.s). UV−visible spectra were recorded on a Kontron Instruments UVIKON 860 spectrometer at 21 °C with a 1 cm path cell. The hydrodynamic radius ($R_H$) was calculated from the Stokes-Einstein equation assuming a spherical model and using pre-determined solvent viscosity values.

Crystallographic Method.

The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N$_2$ stream. X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The crystal-detector distance was 38mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014. The refinement and all further calculations were carried out using SHELXL-2014. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. A semi-empirical absorption correction was applied using SADABS in APEX2, transmission factors: Tmin/Tmax = 0.6655/0.7456. The fluorine atoms F1, F3, F5, F6, F8, F10, F11, F12, F14, F16, F17, F18, F19, F20, F21, F22, F23 and F24 from the counter-anions are disordered over two positions.
2. Synthesis

9-(3-Bromophenyl)-10-methylacridin-10-ium (2\textcdot PF_6)

To a solution of 1,3-dibromobenzene (580 µL, 4.78 mmol, 1 eq) in dry THF (20 mL), was added a 2.5M solution of nBuLi (1.91 mL, 4.78 mmol, 1 eq) in hexanes at –78°C. After 20 minutes at –78°C, 10-methyl-9(10H)-acridone[^1] (1.00 g, 4.78 mmol, 1 eq) was added dropwise. The mixture was further stirred at –78°C for 2 hours, and allowed to room temperature overnight. After addition of a concentrated solution of HCl (37 wt. %) in H_2O (30 mL), the reaction mixture was stirred at RT for 30 min. The solution was poured into an aqueous solution of KPF_6 (6 g in 150 mL). After filtration, the crude product was washed with H_2O (3 x 30 mL). When necessary, the compound was recrystallized from CH_3CN by addition of Et_2O. The desired product was obtained as a yellowish solid in 85% yield (2.01 g).

[^1]: To a solution of 9-(3-bromophenyl)-10-methylacridin-10-ium (206 mg, 0.49 mmol, 1 eq) in dry CH_3OH (20 mL), was added portion wise NaBH_4 (187 mg, 4.96 mmol, 10 eq) at 0°C. The reaction
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

mixture was heated at RT for 16h. After evaporation of solvents, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂). The desired product was obtained as a colorless solid in 72% yield (125 mg). ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.21 – 7.12 (m, 4H, H₃/6-o-p), 7.10 (dd, J = 7.5, 1.5 Hz, 2H, H₁/₈), 6.97 (t, J = 7.5 Hz, 1H, H₆), 6.93 (dt, J = 7.5, 1.5 Hz, 1H, H₀), 6.90 – 6.85 (m, 4H, H₂/₇-4/₅), 5.07 (s, 1H, H₉), 3.33 (s, 3H, N-Me).

To a solution of 9-(3-bromophenyl)-10-methyl-9,10-dihydroacridine (477 mg, 1.36 mmol, 1eq.) and bis(neopentyl glycolato)diboron (338 mg, 1.50 mmol, 1.1 eq.) in dry and degassed DMF (40 mL), were added Pd(dppf)Cl₂ (76 mg, 0.13 mmol, 10%) and KOAc (400 mg, 4.08 mmol, 3 eq). The reaction mixture was heated at 80°C for 16h. After evaporation of solvents, the crude product was obtained as a colorless solid in 76% yield (399 mg). ¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.75 (s, 1H, H₀'), 7.59 (dt, J = 7.0, 1.5 Hz, 1H, H₁), 7.24 – 7.16 (m, 3H, H₃/6-o-p), 7.13 (dd, J = 8.0, 2H, H₁/₈), 7.08 (dt, J = 1.5 Hz, 1H, H₆), 6.95 (d, J = 8.0 Hz, 2H, H₄/₅), 6.89 (td, J = 7.4, 1.1 Hz, 2H, H₂/₇), 5.21 (s, 1H, H₀), 3.74 (s, 4H, CH₂), 3.44 (s, 3H, N-Me), 3.38 (s, 3H, N-Me), 1.34 (s, 6H, Me). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ (ppm) = 144.0 (s, C₉), 142.3 (s, C₁₂/₁₃), 133.2 (s, C₁₀), 132.0 (s, C₁₀), 130.3 (s, C₉), 128.6 (s, C₁₀), 129.7 (s, C₈), 127.9 (s, C₉), 127.1 (s, C₁₁/₁₄), 120.6 (s, C₂/₇), 112.2 (s, C₄/₅), 72.2 (s, C₁₇), 48.6 (s, C₉), 33.1 (s, N-Me), 31.8 (s, C₉), 21.9 (s, Me). MS (ESI-TOF): for C₂₅H₂₅BNO₂, m/z calc = 382.20, m/z found = 382.20 (100%, [M+H]⁺).
Compound (5)

To a solution of 10-methyl-9-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridine (350 mg, 0.88 mmol, 2.1 eq.) and 2,6-dibromopyridine (100 mg, 0.42 mmol, 1 eq.) in degassed DMF (50 mL), was added Pd(PPh₃)₄ (48 mg, 0.09 mmol, 20%) and K₃PO₄ (267 mg, 1.26 mmol, 3 eq.) in degassed DMF (50 mL). The reaction mixture was heated at 80°C for 16h. After evaporation of solvents, the crude product was purified by column chromatography (SiO₂, cyclohexane / CH₂Cl₂ – 7:3). The desired product was obtained as a colorless solid in 87% yield (225 mg).

1H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.93 (t, J = 2.0 Hz, 2H, Hₒ'), 7.88 (dt, J = 8.0, 2.0 Hz, 2H, Hₓ), 7.70 (t, J = 8.0 Hz, 1H, Hᵧ), 7.53 (d, J = 8.0 Hz, 2H, H₁), 7.34 (t, J = 8.0 Hz, 2H, H₂), 7.29 – 7.21 (m, 8H, H₁₋₈), 7.18 (d, J = 8.0 Hz, 2H, Hₒ), 7.01 – 6.90 (m, 8H, H₄₋₇), 3.43 (s, 6H, Me).

13C{¹H} NMR (100 MHz, CDCl₃, 298 K): δ (ppm) = 156.6 (s, Cₓ), 145.0 (s, Cᵧ), 142.5 (s, C₁₂/₁₃), 139.4 (s, Cₓ), 137.2 (s, Cᵧ), 128.7 (s, Cₘ), 128.6 (s, C₃₆), 128.5 (s, Cₒ'), 127.3 (s, C₁/₈), 126.8 (s, C₁₁/₁₄), 126.4 (s, Cₚ), 125.0 (s, Cₓ), 120.7 (s, C₂/₇), 118.3 (s, Cₓ), 112.3 (s, C₄/₆), 48.5 (s, Cₒ), 33.1 (s, Me).

HRMS (ESI-TOF): for C₄₅H₃₆N₃, m/zcalc = 618.2904, m/zfound = 618.2911 (100%, [M+H]+).

Molecular Receptor 1·2PF₆

To a solution of 5 (140 mg, 0.226 mmol, 1 eq.) in DMF (15 mL), was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (206 mg, 0.906 mmol, 4 eq.). The reaction mixture was stirred at room temperature for 16h. The mixture was poured into a saturated solution of KPF₆ (6 g) in H₂O (150 mL), affording a yellowish precipitate. The solution was filtered, washed with H₂O and ethanol. The desired product was obtained as a yellowish solid in 70% yield (143 mg). Characterization of (1·PF₆)⁺: ¹H NMR (600 MHz, CD₃CN, 238 K, 10⁻² mol·L⁻¹): δ (ppm) = 8.42 (d, J = 9.0 Hz, 4H,
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

H₄[5], 8.32 (s, 2H, H₅), 8.17 (dd, J = 9.0, 6.5, 1.5 Hz, 4H, H₃[6]), 7.31 – 7.27 (m, 3H, H₂[7-9]), 7.08 – 7.04 (m, 6H, H₁[8-10]), 6.94 (d, J = 8.0 Hz, 2H, H₁), 6.64 (d, J = 8.0 Hz, 2H, H₄), 6.47 (d, J = 8.0 Hz, 2H, H₅), 4.69 (s, 6H, N-Me). ¹³C NMR (150 MHz, CD₃CN, 238 K, 10⁻² molL⁻¹): 159.8 (s, C₈), 152.5 (s, C₉), 140.3, 138.9 (s, C₃[6]), 136.3, 136.2 (s, C₇), 133.2, 129.3 (s, C₈), 129.2 (s, C₉), 129.0 (s, C₁[8]), 127.5 (s, C₂[7]), 125.9 (s, C₈), 125.3 (s, C₉), 125.2, 118.6 (s, C₄[5]), 118.5 (s, C₅), 38.5 (s, Me). ¹⁹F{¹H} NMR (564 MHz, CD₃CN, 298 K): δ (ppm) = -72.8 (d, J = 706 Hz). ³¹P{¹H} NMR (242 MHz, CD₃CN, 298 K): δ (ppm) = -144.58 (hept, J = 706 Hz). ¹H NMR (500 MHz, D₂O, 298 K): δ (ppm) = 8.47 (d, J = 9.3 Hz, 4H, H₄[5]), 8.40 (s, 2H, H₉), 8.30 – 8.09 (m, 4H, H₃[6]), 7.56 (t, J = 8.0 Hz, 1H, H₆), 7.41 – 7.29 (m, 4H, H₂[7]), 7.26-7.22 (m, 6H, H₁[8-10]), 7.10 (d, J = 7.0 Hz, 2H, H₉), 6.89 (d, J = 7.0 Hz, 2H, H₆), 6.74 (d, J = 8.0 Hz, 2H, H₁), 4.79 (s, 6H, N-Me). ¹³C{¹H} NMR (150 MHz, D₂O, 298 K): δ (ppm) = 160.1, 152.4, 140.3, 138.8 (S, C₃[6]), 135.9 (s, C₇), 135.8, 133.2, 129.7 (s, C₈), 129.0 (s, C₁[8]), 128.9 (s, C₉), 127.0 (s, C₂[7]), 126.4 (s, C₈), 125.2 (s, C₉), 125.1, 118.4 (s, C₅), 118.0 (s, C₄[5]), 37.8 (s, Me). HRMS (ESI-TOF): for C₅₅H₃₃N₅, m/zcalc = 307.6332, m/zfound = 307.6362 (100%, [M]⁺). UV/Vis (CH₃CN, 298 K): λmax (nm) (ε (L.mol⁻¹.cm⁻¹)) = 307 (15300), 348 (15900), 361 (29850), 408 (10350), 425 (11900), 451 (7680). UV/Vis (H₂O, 298 K): λmax (nm) (ε (L.mol⁻¹.cm⁻¹)) = 319 (7400), 325 (7400), 362 (14200), 409 (5300), 431 (5700), 457 (3700). Crystal data for (1)₂·4PF₆: 2(C₄₅H₃₃N₅)₄(F₆P)₂C₂H₅N, orange prism, crystal size 0.36 x 0.34 x 0.28 mm³, monoclinic, space group P 2₁/c, a = 12.8107(4) Å, b = 27.4670(10) Å, c = 25.2827(10) Å, α = 90°, β = 113.746(2)°, γ = 90°, V = 8143.1(5) Å³, Z = 4, ρcalc = 1.511, T = 173(2) K, R(F² > 2σF²) = 0.0977, wR₂ = 0.2449. Out of 87028 reflections a total of 19650 were unique. Crystallographic data (excluding structure factors) for the structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1856039

S5
3. Structural Characterizations of the Synthesized Compounds

Figure S3.1: $^1$H NMR (400 MHz, CD$_3$CN, 298 K) spectrum of 2-PF$_6$.

Figure S3.2: $^1$H NMR (400 MHz, CD$_3$CN, 298 K) spectrum of 2-PF$_6$ (zoom aromatic region).
Figure S3.3: $^{13}$C NMR (100 MHz, CD$_3$CN, 298 K) spectrum of 2-PF$_6$.

Chemical Formula: C$_{20}$H$_{13}$BrN$^+$
Exact Mass: 348.04
Molecular Weight: 349.25

Figure S3.4: MS (ESI-TOF) of 2-PF$_6$. 

S7
Figure S3.5: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 3.

Figure S3.6: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 3 (zoom aromatic region).
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

Figure S3.7: $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) spectrum of 3.

Chemical Formula: C$_{20}$H$_{12}$BrN
Exact Mass: 349.0466
Molecular Weight: 350.2590

Figure S3.8: MS (ESI-TOF) of 3.
Figure S3.9: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 4.

Figure S3.10: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 4 (zoom aromatic region).
Figure S3.11: $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) spectrum of 4.

Chemical Formula: C$_{25}$H$_{26}$BNO$_2$

Exact Mass: 383.2057

Molecular Weight: 383.2980

Figure S3.12: MS (ESI-TOF) of 4.
Figure S3.13: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 5.

Figure S3.14: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 5 (zoom aromatic region).
Figure S3.15: $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) spectrum of 5.

Figure S3.16: MS (ESI-TOF) of 5.
Figure S3.17: $^1$H NMR (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$∙4PF$_6$ ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).

Figure S3.18: $^1$H NMR (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$∙4PF$_6$ ($c = 1\cdot10^{-2}$ mol·L$^{-1}$; zoom aromatic region).
Figure S3.19: $^{13}$C NMR (150 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$$\cdot$4PF$_6$ ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).

Figure S3.20: $^1$H--$^1$H COSY 2D-spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$$\cdot$4PF$_6$ ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).
Figure S3.21: $^1$H–$^{13}$C HSQC 2D-spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$·4PF$_6$ ($c = 1 \cdot 10^{-2}$ mol·L$^{-1}$).

Figure S3.22: $^1$H–$^{13}$C HMBC 2D-spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)$_2$·4PF$_6$ ($c = 1 \cdot 10^{-2}$ mol·L$^{-1}$).
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

Figure S3.23: $^1$H–$^1$H NOESY 2D-spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of the dimer of (1)·4PF$_6$ ($c = 1 \cdot 10^{-2}$ mol·L$^{-1}$).

Figure S3.24: $^1$H NMR (600 MHz, CD$_3$CN, 298 K) spectrum of the monomer of (1)·4PF$_6$ ($c = 5 \cdot 10^{-4}$ mol·L$^{-1}$).
Figure S3.25: $^1$H NMR (600 MHz, CD$_3$CN, 298 K) spectrum of the monomer of 1·2PF$_6$ ($c = 5\cdot10^{-4}$ mol·L$^{-1}$; zoom aromatic region).

Figure S3.26: $^1$H NMR (600 MHz, D$_2$O, 298 K) spectrum of the dimer of (1)2·4Cl ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

Figure S3.27: $^1$H NMR (600 MHz, D$_2$O, 298 K) spectrum of the dimer of (1)$_2$·4Cl ($c = 1\times10^{-2}$ mol·L$^{-1}$; zoom aromatic region).

Figure S3.28: $^{13}$C NMR (150 MHz, D$_2$O, 298 K) spectrum of the dimer of (1)$_2$·4Cl ($c = 1\times10^{-2}$ mol·L$^{-1}$).
Figure S3.29: $^1$H–$^1$H COSY 2D-spectrum (600 MHz, D$_2$O, 298 K) of the dimer of (1)$_2$·4Cl ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).

Figure S3.30: $^1$H–$^1$H HSQC 2D-spectrum (600 MHz, D$_2$O, 298 K) of the dimer of (1)$_2$·4Cl ($c = 1\cdot10^{-2}$ mol·L$^{-1}$).
Figure S3.31: $^1$H–$^1$H HMBC 2D-spectrum (600 MHz, D$_2$O, 298 K) of the dimer of (1)$_2$·4Cl ($c = 1 \cdot 10^{-2}$ mol·L$^{-1}$).

Figure S3.32: $^1$H–$^1$H NOESY 2D-spectrum (600 MHz, D$_2$O, 298 K) of the dimer of (1)$_2$·4Cl ($c = 1 \cdot 10^{-2}$ mol·L$^{-1}$).
Electronic Supporting Information

Figure S3.33: MS (ESI-TOF) of 1·2PF₆.

Figure S3.34: ¹H NMR spectra (400 MHz, CD₃CN, 343 K) of 1·2PF₆ at 1·10⁻², 5·10⁻³, 1·10⁻³, 5·10⁻⁴ mol·L⁻¹.
Figure S3.35: $^1$H NMR spectra (400 MHz, CD$_3$CN, 298 K) of 1·2PF$_6$ at 1·10$^{-2}$, 5·10$^{-3}$, 1·10$^{-3}$, 5·10$^{-4}$ mol·L$^{-1}$.

Figure S3.36: $^1$H NMR spectra (400 MHz, CD$_3$CN, 248 K) of 1·2PF$_6$ at 1·10$^{-2}$, 5·10$^{-3}$, 1·10$^{-3}$, 5·10$^{-4}$ mol·L$^{-1}$.
Figure S3.37: $^1$H NMR spectra (400 MHz, D$_2$O, 298 K) of (1)$_2$·4Cl at 1·10$^{-2}$, 5·10$^{-3}$, 1·10$^{-3}$, 5·10$^{-4}$ mol·L$^{-1}$.

Figure S3.38: $^1$H DOSY spectrum (600 MHz, CD$_3$CN, 298 K) spectrum of 1·2PF$_6$ at 5·10$^{-4}$ mol·L$^{-1}$. 
Figure S3.39: $^1$H DOSY spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of 1-2PF$_6$ at $5 \cdot 10^{-4}$ mol·L$^{-1}$.

Figure S3.40: $^1$H DOSY spectrum (600 MHz, CD$_3$CN, 238 K) spectrum of 1-2PF$_6$ at $1 \cdot 10^{-2}$ mol·L$^{-1}$.
Figure S3.41: $^1$H DOSY spectrum (600 MHz, D$_2$O, 298 K) spectrum of (1)$_2$∙4Cl at 1∙10$^{-2}$ mol∙L$^{-1}$.

Figure S3.42: $^1$H NMR (500 MHz, 298 K, $c = 3\cdot10^{-3}$ mol∙L$^{-1}$) spectra of 1.2PF$_6$ from pure CD$_3$CN to pure DMSO-$d_6$. 

S26
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

**Figure S3.43:** $^1\text{H}$ NMR (400 MHz, CD$_3$CN, 298 K) spectra of a) the triphenyl-*bis*-acridinium receptor[S1] and b) 1∙2PF$_6$ (c = 5∙10$^{-4}$ mol∙L$^{-1}$).

**Figure S3.44:** $^1\text{H}$ NMR (400 MHz, CD$_3$CN, 298 K) spectra of a) the triphenyl-*bis*-acridinium receptor[S1] and b) 1∙2PF$_6$ (c = 5∙10$^{-4}$ mol∙L$^{-1}$; zoom of the aromatic region).
Figure S3.45: Mass Spectra (ESI-TOF) of a solution of 1·2PF₆ in CH₂CN injected at different concentrations: 1·10⁻³, 1·10⁻⁴, 1·10⁻⁵ mol·L⁻¹ (zoom on the aggregate region).

Figure S3.46: ¹H NMR (600 MHz, D₂O) spectra of (1)∙⁴Cl recorded from 298 K to 358 K.
**Figure S3.47:** $^1$H NMR (600 MHz, CD$_3$CN) spectra of 1·2Cl recorded from 238 K to 348 K ($c = 1.10^{-2}$ mol·L$\text{⁻}^{1}$).

**Figure S3.48:** $^1$H DOSY spectrum (300 MHz, CD$_3$CN, 238 K) spectrum of (1)2·4PF$_6$ at 1·10$^{-2}$ mol·L$\text{⁻}^{1}$.
**Figure S3.49:** $^{19}$F DOSY spectrum (300 MHz, CD$_3$CN, 238 K) spectrum of (1)$_2$·4PF$_6$ at $1 \cdot 10^{-2}$ mol·L$^{-1}$.

**Figure S3.50:** $^{19}$F DOSY spectrum (300 MHz, CD$_3$CN, 238 K) spectrum of KPF$_6$ at $1 \cdot 10^{-2}$ mol·L$^{-1}$. 
4. UV-Vis Characterizations of 1.2PF₆

![UV-Vis spectra](image)

**Figure S4.1:** UV-Vis spectrum (CH₃CN, $l = 0.1$ cm, 298 K) of 1.2PF₆ (blue, $c = 5 \times 10^{-4}$ mol·L⁻¹).

![UV-Vis spectra](image)

**Figure S4.2:** UV-Vis spectra (CH₃CN, $l = 0.1$ cm, 298 K) of 1.2PF₆ (blue, $c = 5 \times 10^{-4}$ mol·L⁻¹), 2,6-diphenylpyridine (purple, $c = 5 \times 10^{-4}$ mol·L⁻¹), 9-phenyl-N-acridinium (red, $c = 5 \times 10^{-4}$ mol·L⁻¹) and the sum of 2,6-diphenylpyridine and twice of 9-phenyl-N-acridinium (light blue).
Figure S4.3: UV-Vis spectrum (H$_2$O, $l = 0.1$ cm, 298 K) of (1)$_2$·4Cl (blue, $c = 5\cdot10^{-4}$ mol·L$^{-1}$).

5. Crystallographic Data of (1)$_2$·4PF$_6$

Within the crystal lattice, the dimers are orientated in a head-to-tail manner along the median of the $b$ and $c$ axis. Dimers of 1·2PF$_6$ are arranged according to a herringbone structure along the $b$ and $c$ axis and are organized in a ladder type manner along the $a$ axis.

Figure S5.1: Representation of the crystal packing along the $a$ axis.
Entwined Dimers Formation from Self-Complementary bis-Acridiniums

Figure S5.2: Representation of the crystal packing along the $b$ axis.

Figure S5.3: Representation of the crystal packing along the $c$ axis.

6. References


