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A Chemically-Responsive bis-Acridinium Receptor

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A dicationic receptor based on two acridinium moieties linked by a triphenylene spacer has been studied in solution and in the solid state. The recognition moieties, namely acridiniums, have been exploited to evidence a host-guest response of the receptor with electron rich guests. Upon addition of methoxide anions, the formation of the bis-acridane form of the receptor has been observed. The chemical responsiveness of the receptor to these anions inhibits its recognition properties towards *π*-donor guests. In addition, the reversibility of the chemical response has been demonstrated under acidic conditions.

Introduction

Molecular switches are systems changing their chemical and physico-chemical properties (colorimetric/fluorometric, conductivity, etc.) as the result of external stimuli (light, protons, metal cations, anions, temperature, etc.) The most common switches incorporate photo- and/or electroresponsive species such as dimethyldihydropyrene,¹ spiropyran² and diarylethene.³ These components form a unique class of building blocks that hold promise for emerging applications in molecular electronics and smart material design.⁴ The logical evolution of these materials will be their incorporation in supramolecular architectures in order to favour (or disfavour) weak interactions between different components thus paving the path to a new generation of receptors.

Non-covalent and weak forces, such as π - π stacking interactions are fundamental interactions for biological systems. For example, these interactions combined with hydrogen bonds ensure the three-dimensional organization of double-strand architectures whereas they can engender diseases when polyaromatics intercalate in between two nucleobases of DNA. As a result, chemists have devoted

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numerous efforts to synthesize a number of systems in order to understand and control these interactions.^{5,6,7} Among these systems, molecular tweezers are an important class of molecules⁸ wherein two recognition units are pre-organized to interact with organic and inorganic polyaromatic guests.⁹

Since the pioneer work of Zimmerman and his co-workers,¹⁰ 9phenyl-acridines¹¹ and their positively charged counterparts, namely 9-phenyl-N-acridiniums,¹² have been used for the recognition of electron rich aromatic guests. However, until now the switching ability of the 9-phenyl-N-acridinium has been scarcely exploited in the field of supramolecular chemistry.¹³ The photo switching properties of the 9-phenyl-*N*acridiniums was used to trigger the motion of a crown ether macrocycle in a family of rotaxanes.^{13a-c} More recently, 9phenyl-N-acridiniums were incorporated into the structure of a chemically-switchable polyaromatic macrocycle to reversibly bind long hydrophilic molecules in water.^{13d} The 9-phenyl-Nacridinium building block show several mesomeric forms and two of them exhibit i) a pyridinium central core and ii) a triarylium motif (Scheme 1). Like triarylmethane dyes (e.g. malachite green),¹⁴ they demonstrate chemically-responsive behaviour.¹⁵ The positive charge of the 9-phenyl-*N*-acridiniums can formally be seen as localized on the carbon at the 9position. Therefore, the addition of a hydroxide ion leads to the formation of an acridane derivative, this reaction being reversible under acidic conditions.

HO Pyridinium Triarylium Acridane Mesomeric Form

Mesomeric Form



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Scheme 1. Two possible mesomeric forms of the 9-phenyl-N-methyl acridinium molecule showing the regioselective addition of HO⁻ anion.

In this report, we focused on understanding the different physicochemical and supramolecular recognition properties of a new molecular system incorporating two acridinium subunits connected by a triphenylene spacer. By organizing the two acridinium units, we expected to observe molecular recognition properties and to modulate them by a chemical stimulus thanks to the chemical responsiveness of the acridinium moiety. Herein, we describe i) the synthesis of the receptor **1.2PF**₆, ii) its solid state characterization, iii) its response to a chemical stimulus and iv) its recognition properties in solution towards π -donors and its potential as a switchable receptor.

Results and discussion

Synthesis

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The synthesis of the target molecule 1.2PF₆ bearing two acridinium units was performed in three synthetic steps as shown in Scheme 2. First, the functionalization of 1,3dibromobenzene with bis(pinacolato)diboron was carried out under Suzuki-Miyaura conditions using Pd(dppf)Cl₂ as catalyst and KOAc as base. After purification by column chromatography. 1,3-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)benzene (2) was isolated in 89% yield.¹⁶ Compound 2 was then reacted with 1,3-dibromobenzene (3 eq.) in DMF under Suzuki cross-coupling conditions using Pd(PPh₃)₄ as catalyst (20%) and K₃PO₄ (3 eq.) as base. The 3,3"dibromo-1,1':3',1"-terphenyl (3) was isolated in 59% yield. Finally, introduction of the acridinium units was performed by metal-halogen exchange of 3 using a 2.5M solution of n-BuLi in hexanes, then followed by addition of 10-methyl-9(10H)acridone¹⁷ at -78°C (2 eq.). Acidification of the reaction mixture with a 2N solution of HCl in H₂O afforded the bisacridinium compound as chloride salt (1.2Cl) which was further converted to the hexafluorophosphate salt by anion metathesis using KPF_6 . After filtration, the receptor (1.2PF₆) was obtained as a yellow solid in 87 % yield.



Scheme 2. Synthesis of the *bis*(acridylium) receptor (1.2PF₆) from 1,3-dibromobenzene as starting material: (i) *bis*(pinacolato)diboron (2.5 eq.), Pd(dppf)Cl₂ (10%), KOAc (3 eq.), DMF, 80°C, 16 h (89%); (iii) 1,3-dibromobenzene (3 eq.), Pd(PPh₃)₄ (20%), K₃PO₄ (3 eq.), DMF, 80°C, 16 h (59%); (iii) a) *n*-BuLi (2.1 eq.), THF, -78° C, 30 min, b) 10-methyl-9(10H)-acridone (2.2 eq.), -78° C to RT, 16h, c) HCl (2N), H₂O, 30 min, d) KPF₆(s), H₂O, RT (87%).

Solid State Structure

Suitable single crystals for X-ray diffraction were grown by slow vapor diffusion of Et₂O into a concentrated solution of 1.2PF₆ in CH₃CN.¹⁸ The receptor 1.2PF₆ adopts a U-shaped conformation in the solid state (Figure 1). This U-shaped conformation is favoured by the inclusion of a PF₆ counterion. In this conformation the acridinium subunits are positioned in two quasi parallel planes (offset angle of 7.34°). As a result of this organization, the C9-C9 and N-N distances values within a molecule are close (7.804 Å and 8.127 Å respectively). The included PF₆⁻ counter-ion interacts with both acridiniums of 1.2PF₆ through [C•••F] close contacts of 3.111 Å for the shortest distance. The induced-fit ability of the receptor was rendered possible on account of the torsion angle existing with the triphenyl spacer, 111.18° and 93.52°. This observation is the result of the steric hindrance existing between the protons at the 1- and 8- positions of the acridinium units and the adjacent protons of the spacer. The triphenyl spacer shows an out-of-plane distortion of its central phenyl as the result of the steric hindrance existing between the central C-H pointing towards the cavity and the two corresponding C-H of the two external phenyls. The crystal packing (see ESI, Fig. S7) shows that the molecules of 1.2PF₆ are aligned in a top-to-tail arrangement along c axis and according to a ladder type structure along the median of the *a* and b axis. Noteworthy, the second PF_6^- counter-ion is located in between two cavities of two acridiniums of two different molecules of 1.2PF₆ as the result of [CH•••F] close contacts of 2.406 Å thus providing additional interactions for the crystal stabilization.



Figure 1. Solid state structure of the receptor **1.2PF**₆. a) Scheme of the **1.2PF**₆. b) Side view of the receptor showing the **U**-shape conformation and the inclusion of a PF₆⁻ counter-ion inside the cavity formed by the two acridinium units. c) Top view of the receptor showing the distortion of the triphenvl linker.

The calculated optimized geometry with two PF_6^- was also found to be the **U**-shaped conformation with one PF_6^- included between the two acridinium units (Figure 2). This observation confirmed the stabilizing electrostatic interactions between the PF_6^- anion and positively charged acridinium arms. As illustrated in Figure 2, the C9-C9 and N-N distances were calculated to be 7.91 Å and 8.12 Å in **1.2PF_6** and 7.98 Å and 8.57 Å in **1**²⁺. All these values are in excellent agreement with the X-ray structure (7.804 Å and 8.127 Å, respectively).



Figure 2. Optimized U-shaped conformations of (a) 1.2PF₆ and (b) bis-acridinium 1²⁺

Solution Studies

The conformations of receptor $1.2PF_6$ were also studied in solution by a combination of 1D (¹H, ¹³C, ¹⁹F and ³¹P) and 2D (namely COSY, HSQC and HMBC) NMR experiments. The ¹H NMR spectrum of $1.2PF_6$ in acetone- d^6 reveals sharp signals in the aromatic region in agreement with free rotations in $1.2 PF_6$ thus witnessing the relatively low rotation barrier between the different conformers of the molecule (fast exchange regime, Figure 3a). Upon cooling, a broadening of all ¹H signals are observed on account of the slower rotations in both 9-phenyl-N-acridinium moieties and the triphenyl linker which corresponds to the intermediate exchange regime (Figure 3b and ESI, Figure S3.23). At 193 K (lowest temperature reachable in acetone- d^{\flat}) no rotational freezing was observed at the NMR timescale. In an attempt to reach the slow exchange regime, increasing of the applied field from 400 to 600 MHz did not lead to a simplification of the NMR spectrum at low temperature (Figure S3.24). This observation suggests a low rotational barrier between the different conformers of 1.2PF₆.



Figure 3. Partial ¹H NMR (400 MHz, Acetone-d⁶) spectra of **1.2PF**₆ at 298 K (top spectrum) and 208 K (bottom spectrum). The red arrows indicate the fast free rotation around the C-C bonds at 298K.

The various conformations of the isolated *bis*-acridinium compound $\mathbf{1}^{2^+}$ were further investigated by DFT calculations (Figure 4). As the result of the variation of the torsion angles (α , β , γ , and δ dihedral angles, Figure 4 and Table S6.1), $\mathbf{1}^{2^+}$ can adopt several conformations. In its most stable conformation, $\mathbf{1}^{2^+}$ shows a **T**-shaped geometry (edge to face interactions between the two acridylium moieties) while the **U**-shaped

geometry is less stable by 10.3 kJ.mol⁻¹. This result is consistent with general findings for aromatic-aromatic interactions.¹⁹ Other conformations, namely **S**-shaped and **W**-shaped, were obtained by varying the β and γ dihedral angles. Their energies were found to be similar to the **U**-shaped conformation suggesting that the interaction between both acridiniums is negligible. These results are in agreement with the low rotational barrier observed in the VT NMR studies.



Figure 4. Local minima of $1.2PF_6$ obtained by varying the dihedral angles ($\alpha, \beta, \gamma, \delta$); DFT calculations (top) and their corresponding representative schemes (bottom).

Chemical Response

We were interested in probing the chemical responsive properties of 1.2PF₆. Upon addition of 2 eq. of tetrabutylammonium hydroxide (TBAOH), immediate bleaching of the yellowish solution of 1.2PF₆ was observed with the formation of a precipitate. The dihydroxylated acridane was not soluble enough to allow its full characterization by NMR spectroscopy in most common NMR solvents. As a consequence, 1.2PF₆ was converted into its more soluble dimethoxylated derivative 4. The receptor 1.2PF₆ was reacted in methanol with K_2CO_3 (3.3 eq) to afford the desired bis-acridane 4 as a white solid in guantitative yield (see ESI). As expected, the ¹H spectrum in DMSO- d^6 of **4** shows a dearomatization of the acridinium moieties compared to **1.2PF**₆ (Figure 5b). Large upfield shifts of the characteristic signals of the acridinium subunits were monitored ($\Delta H_{1/8}$ = 0.80 ppm, $\Delta H_{2/7}$ = 0.62 ppm, $\Delta H_{3/6}$ = 1.52 ppm and $\Delta H_{4/5}$ = 1.60 ppm) reflecting the disappearance of their positive charges. An analogous upfield shift was observed for the methyl protons ($\Delta Me = 1.43$ ppm) which is consistent with the loss of aromaticity of the acridinium cores. Additionally, a new singlet appears at 3.51 ppm assigned to the methoxy protons of the newly formed acridane. Upon addition of 2 eq. of trifluoroacetic acid (TFA), the original 1 H NMR spectrum of $\mathbf{1}^{2+}$ was restored. This observation can be rationalized by the elimination of two methanol molecules (δ = 3.16 ppm, Figure 5c) leading to the re-aromatization of the acridinium cores.



Figure 5. Partial ¹H NMR (400 MHz, DMSO- d^6 , 298 K) spectra of (a) **1.2PF**₆ ($c = 5.10^{-3}$ mol.l⁻¹) and **4** ($c = 5.10^{-3}$ mol.l⁻¹) before (b) and after (c) addition of 2 eq. of TFA.

The switching was also monitored by UV-Vis spectroscopy. The optical spectrum of 1.2PF₆ (Figure 6) shows five maxima at 337 $(\varepsilon = 17000 \text{ L.mol}^{-1}.\text{cm}^{-1}), 360 (31150), 397 (11200), 426$ (12450) and 450 nm (8300) in DMF. These transitions were in agreement with the reported wavelengths in litterature²⁰ and reflect a linear superposition of the absorption of two 9phenyl-N-acridinium subunits in 1.2PF₆. In other words, no additional transitions were detected compared to a 9-phenyl-N-acridinium moiety thus demonstrating that no electronic coupling occurs in these conditions between the two subunits. Calculations carried out on 1^{2+} using TD-DFT method were performed to gain insight into the nature of the two first lowenergy bands (Table S6.2). The first dipole-allowed absorption is predicted at 411 nm, a value in remarkable agreement with experiments (ca. 425 nm). This transition is predicted to arise from a mixing of one-electron excitations from HOMO-2 and HOMO-3 to the LUMO and LUMO+1 (Figure S6.1). The quasidegenerated two HOMOs and two LUMOs are localized on a different acridinium units. This transition is mainly due to localized π - π * electronic excitation on each aromatic unit. A second transition is calculated at 364 nm very close to the experimental value recorded at 360 nm. This transition is assigned from a mixing of H–5 \rightarrow L and H–4 \rightarrow L+1 excitations corresponding to a charge transfer from a phenylene unit of the central bridge to the acridinium units.

In comparison, the UV–Vis spectrum of **4** shows an absorbance only in the UV region at 275 (30300), 310 (9500) and 326 nm (7600) as depicted in Figure 5. Upon addition of an excess of TFA (40 eq.), full restoration of the optical spectrum of $\mathbf{1}^{2+}$ was observed with the appearance of the maxima at 360, 397, 426 and 450 nm.



Figure 6. UV-Vis spectra of a solution (DMF, $c = 4.10^{-5}$ mol.L⁻¹, l = 1 cm) of **4** before (red) and after addition of excess of TFA (blue) and a solution of **1.2PF₆** (blue dashed line).

These observations can be best interpreted in terms of the regeneration of $\mathbf{1}^{2+}$ as the result of the loss of two methanol molecules leading to the rearomatization of the acridinium cores. In conclusion, $\mathbf{1.2PF}_6$ presents reversible chemiochromic properties coming from the clean conversion between its aromatic acridinium form (absorbing in the visible region) and its non-aromatic acridane form (absorbing in the near UV region).

Host-Guest Response

As shown in the X-ray structure, the large distance between the acridinium units allows the inclusion of a planar and π conjugated guest. Although the average distance (7.95 Å) between the two acridinium subunits was found in solid state (vide supra) to be above the optimum distance (7 Å) for π - π stacking interactions, we were interested in probing inclusion complex formation in solution through π - π stacking interactions using two electron-rich guests, namely tetrathiafulvalene (TTF) and pyrene. Shifts for all signals of **1.2PF**₆ were observed in ¹H NMR upon addition of small aliquots of a stock solution of the guests in CDCl₃ to a solution of $1.2PF_6$ ($c = 10^{-2}$ mol.L⁻¹) in CD₃CN (Figure S4.1). As depicted in Figure 6 using TTF as guest, π - π interactions between the guest and the acridinium subunits is evidenced by the upfield shift of the acridinium protons ($\Delta H_{1/8}$ = 0.12 ppm, $\Delta H_{2/7}$ = 0.09 ppm, $\Delta H_{3/6}$ = 0.11 ppm and $\Delta H_{4/5}$ = 0.12 ppm respectively) upon addition of 7 eq. of TTF. The inclusion of TTF was confirmed by the downfield shifts of the inner protons of the triphenyl spacer ($\Delta H = 0.04$ and 0.02 ppm respectively). Noteworthy, the TTF signal at 6.2 ppm is broadened as the result of its dynamic complexation on the NMR timescale (see ESI, Figure S4.3). In a similar manner, upfield shifts of the acridinium protons ($\Delta H_{1/8}$ = 0.31 ppm, $\Delta H_{2/7}$ = 0.14 ppm, $\Delta H_{3/6}$ = 0.43 ppm and $\Delta H_{4/5}$ = 0.29 ppm respectively) are observed upon addition of 15 eq. of pyrene. The chemical shifts of the pyrene protons are also shifted upfield ($\Delta H_{1/3/6/8}$ = 0.02, $\Delta H_{2/7}$ = 0.02 and $\Delta H_{4/5/9/10}$ = 0.01 ppm) as the result of the interaction of pyrene with **1.2PF**₆.

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The more pronounced shifts of the acridinium protons compared to the triphenyl spacer protons can be explained by the closer proximity of the guest to the charged moieties on account of π - π interactions. These effects were confirmed by DFT calculations indicating an intercalation of the TTF guest between two acridinium units (Figure 7). The optimized geometry of the inclusion complex TTF 1^{2+} reveals that the receptor $\mathbf{1}^{2+}$ adapts to the guest. The noticeable feature is a shortening of the characteristic N-N and C9-C9 distances (from 8.57 to 7.10 Å and from 7.98 to 7.34 Å, respectively) when compared to its isolated counterpart reflecting the interaction between $\mathbf{1}^{2+}$ and TTF. The electrostatic potential of $\mathbf{1}^{2+}$ exhibits a strong negative potential in the vicinity of acridinium units and a more positive potential on the central phenylene of the bridge (Figure 7b). The TTF shows positive potential consistent with its electron rich character. As a consequence, the overlap between the positive potential of TTF with the negative potential of the two acridiniums units is responsible for the electrostatic stabilization upon complexation (Figure 7c). The interaction of TTF with 1^{2+} is also confirmed by i) the analysis of non-covalent interactions showing large attractive area between planar aromatic rings (Figure S6.2) and ii) by the total interaction energy calculated to be -123.3 kJ.mol⁻¹. The association constants with TTF and pyrene, fitted to a 1:1 binding model by NMR,²¹ were found to be similar ($Ka \approx 10 \text{ M}^-$ ¹) for both guests. This rather low binding constant can be rationalized by i) the acridinium-acridinium distance found to be slightly above the optimum distance for π - π stacking in the solid state structure of 1.2PF₆ (7.95 Å), ii) the relative flexibility of the triphenyl spacer and iii) the low energy barrier between conformers leading to very different relative orientations of both acridiniums in solution. Moreover, larger binding constants could be expected by increasing the π overlap between the host and the guest such as in the case of porphyrin tweezers.^{8e,23} As control experiments, titrations have been carried out using 9-phenyl-N-acridinium monomer as host. As expected, no binding affinity was observed for either the TTF or pyrene guests thus suggesting a cooperative assistance between the two acridinium moieties in 1.2PF₆ even if the binding constant are rather low. This cooperative effect can also be confirmed by the color change observation upon addition of guests to a solution of 1.2PF₆ (see ESI, Figures S5.3 and S5.5, from yellowish to greenish solution for TTF 1^{2+} and to orange solution for Pyrene 1^{2+}). These colour changes are the result of the appearance of new absorption bands in the visible region of the spectra. These bands are absent in the absorption spectra of the sum of the equimolar mixture of host and guest. As a consequence, they can be attributed to a charge transfer from the electron rich guest to the electron poor receptor. The Ka values were found to be similar to the Ka values found by NMR titrations for both guests, fitted to a 1:1 binding model.



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Figure 7. Electrostatic potential surface of a) the isolated **TTF**, b) the receptor 1^{2^+} and c) the TTF 1^{2^+} inclusion complex. d) Optimized geometry of the TTF 1^{2^+} inclusion complex (ω B97xD/6-31G(d) calculations).

We were interested in probing the recognition properties of **4**. ¹H NMR titration experiments were performed in $CDCl_3$ using both guests. As expected, no binding was observed with *bis*acridane **4** derivative as host as the result of the dearomatization of the acridinium core. This observation is a proof of concept of a modulation of the binding of this *bis*acridinium receptor by a chemical stimulus.

Conclusions

The synthesis of a molecular receptor bearing two acridiniums connected to a triphenyl spacer has been described. It exhibits recognition properties in the solid state as well as in solution. In the solid state, the receptor adopts a U-shaped structure on account of the formation of an inclusion complex with one hexafluorophosphate counter-ion. NMR titrations have revealed the recognition properties of 1.2PF₆ in solution with electron donor guests (perylene, TTF) through π - π stacking. The receptor has also shown its ability to reversibly respond to a chemical stimulus and to modify its structure upon addition of nucleophiles (HO⁻, CH₃O⁻) leading to its *bis*-acridane form. In this form, the receptor does not exhibit any recognition properties. Moreover, the chemical response can be best interpreted in terms of chemiochromic response as demonstrated by the changes in the optical spectra. Finally, DFT calculations shed light on the electronic states of our receptor. Work is underway to design and synthesize a new receptor incorporating two acridiniums with enhanced switchable receptor properties.

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Experimental Section

Materials, syntheses and general procedures of the target molecule **1.2PF**₆, including 10-methyl-9(10H)-acridone¹⁷ and 1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene (2),¹⁶ are provided in the ESI. All compounds were synthesized using Schlenk technics and were fully characterized by 1D (¹H, $^{13}C{^{1}H}$, $^{31}P{^{1}H}$ and $^{19}F{^{1}H}$ and 2D (COSY, HSQC and HMBC) NMR experiments and by mass spectrometry experiments. NMR experiments were monitored at 400 MHz, on a Bruker Advance III 400 at 298 K unless specified by other means. Mass spectra (MS) were obtained using gas chromatography (Finnigan Trace GC Ultra, Thermo Electron) coupled to a mass spectrometer (Finnigan Trace DSQ, Thermo Electron) (GC-MS). UV-Vis. Spectra were recorded on a Cary 500 spectrometer and on a Perkin Elmer Lambda 1050 equipped with a 3D WB detector module in the range 250-800 nm. A single crystal of the compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the WinGX suite of programs,²⁴ the structure was solved with ShelxT²⁵ program and refined by fullmatrix least-squares methods using SHELXL-14.²⁶ All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined with a riding model. A model of disorder was introduced for a PF_6^- anion and for an acetonitrile molecule. The inability of DFT method to correctly account for dispersive interactions is well known. This problem is due to the fact that dispersion forces result from long-range correlations between electrons, whereas some of the current exchange-correlation potentials model only local correlation effects. Several improvements to correct the drawbacks of first functionals have been proposed. We used in this paper the long range corrected ω B97XD functional that allow an accurate description of systems involving noncovalent interactions with strong dispersion effects with a moderate computational cost. All ab initio simulations have been achieved with the GAUSSIAN09 program,²⁷ applying default procedures, integration grids, algorithms and parameters, except when noted. The geometries of the studied compounds were optimized using both the ω B97XD²⁸ hybrid exchange correlation functional and the standard 6-31G* basis set.²⁹ We have systematically computed the vibrational spectrum on the minimized structures to check that there is no imaginary vibrational mode. The complexation energies between 1 and TTF have been estimated by energy difference between the complex and the sum of the isolated constituents. The complexation energy was corrected from the basis set superposition errors (BSSE) using the standard counterpoise (CP) approach. The modelling of bulk solvent effects (here acetonitrile, as in the experiments) is included through the Polarizable Continuum Model (PCM). The accuracy of the different DFT functionals (such as PBEO, BLYP, CAM-B3LYP, HSEH1PBE, LC-@PBE, @B97XD, M06 and M062X) for the optical properties have been explored by performing

benchmark calculations for the $\mathbf{1}^{\mathbf{2}^{+}}$ in an water environment and the calculated absorption energies are summarized in Table S6.2 of the ESI. As can be seen from Table S6.2 (ESI), the M06 method gives the absorption energies in excellent agreement with experiment. Hence, the M06 functional was used to calculate the lowest singlet transitions from the optimized geometry calculated with ω B97XD for all the studied compounds.

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- 18 Crystal data for 1.2PF_6 : $C_{46}\text{H}_{34}\text{N}_2,2(\text{PF}_6),2(\text{C}_2\text{H}_3\text{N})$, yellow needle, crystal size $0.25 \times 0.12 \times 0.11 \text{ mm}^3$, triclinic, space group P-1, a = 7.9128(6) Å; b = 16.8566(1) Å; c = 17.3103(1)Å; $\alpha = 88.592(2)^\circ$; $\beta = 88.414(2)^\circ$; $\gamma = 82.929(2)^\circ$; V = 2289.94Å³, Z = 2, $\rho_{calcd} = 1.432$, T = 200(2) K, $R1(F2 > 2\sigma F2) = 0.0470$, wR2 = 0.1289. Out of 78626 reflection a total of 13455 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–1560847.

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The recognition and the chemical-response properties of a *bis*-acridinium triphenylene receptor have been investigated.

