Supporting Information for

Redox- and pH-responsive orthogonal supramolecular self-assembly: An ensemble displaying molecular switching characteristics

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I. Materials and methods

All reagents were purchased from Aldrich and used without further purification. Compounds **1** and **2** were prepared according to reported procedures.[1,2] Except where noted, all measurements were performed in a mixture of $CH(D)Cl_3$, CS_2 (7:3, v/v) containing a trace amount of (deuterated) DMSO so as to overcome the limited solubility of compound **2**. 1D ^{1}H, 2D ^{1}H ROESY and DOSY NMR spectra were recorded at 25 ^{o}C using 400 MHz Agilent MR or 600 MHz Varian DirectDrive instruments. DOSY spectra were referenced relative to D_2O/H_2O at 25 ^{o}C. UV-Vis spectra were recorded from 400 to 800 nm using a Varian Cary 5000 spectrophotometer at room temperature. For the spectral titrations, changes in spectral signature were monitored at one or more wavelengths as a function of the appropriate parameter (concentration, mole fraction, etc.). Unless otherwise indicated, a cell length of 10 mm was used for all UV-Vis spectral studies. Cyclic voltammetry (CV) measurements were carried out at ambient temperature using a CV-50W voltammetric analyzer (BAS). All CV measurements were performed with three electrodes at room temperature, namely a glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl couple as the reference electrode. All solutions were purged with nitrogen for 5 min before each electrochemical experiment. A scan rate of 10 mV/*s* was employed for all measurements. For spectroelectrochemical analyses, a Pt mesh working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode were used. The diffusion coefficients, *D*, of SPr-TTF-pyrrole, **3**[3] and **1** were measured by chronoamperometry on a Au microelectrode (radius, a = 50 μm).[4] For this measurement, a CH 900 potentiostat (CH Instrument, TX) was used. Dynamic light scattering (DLS) was conducted with a Wyatt DynaPro NanoStar equipped with a 100 mW, 662 nm air-launched laser and a detector at a constant angle of 90°.

II. ^{1}H NMR spectroscopic analyses

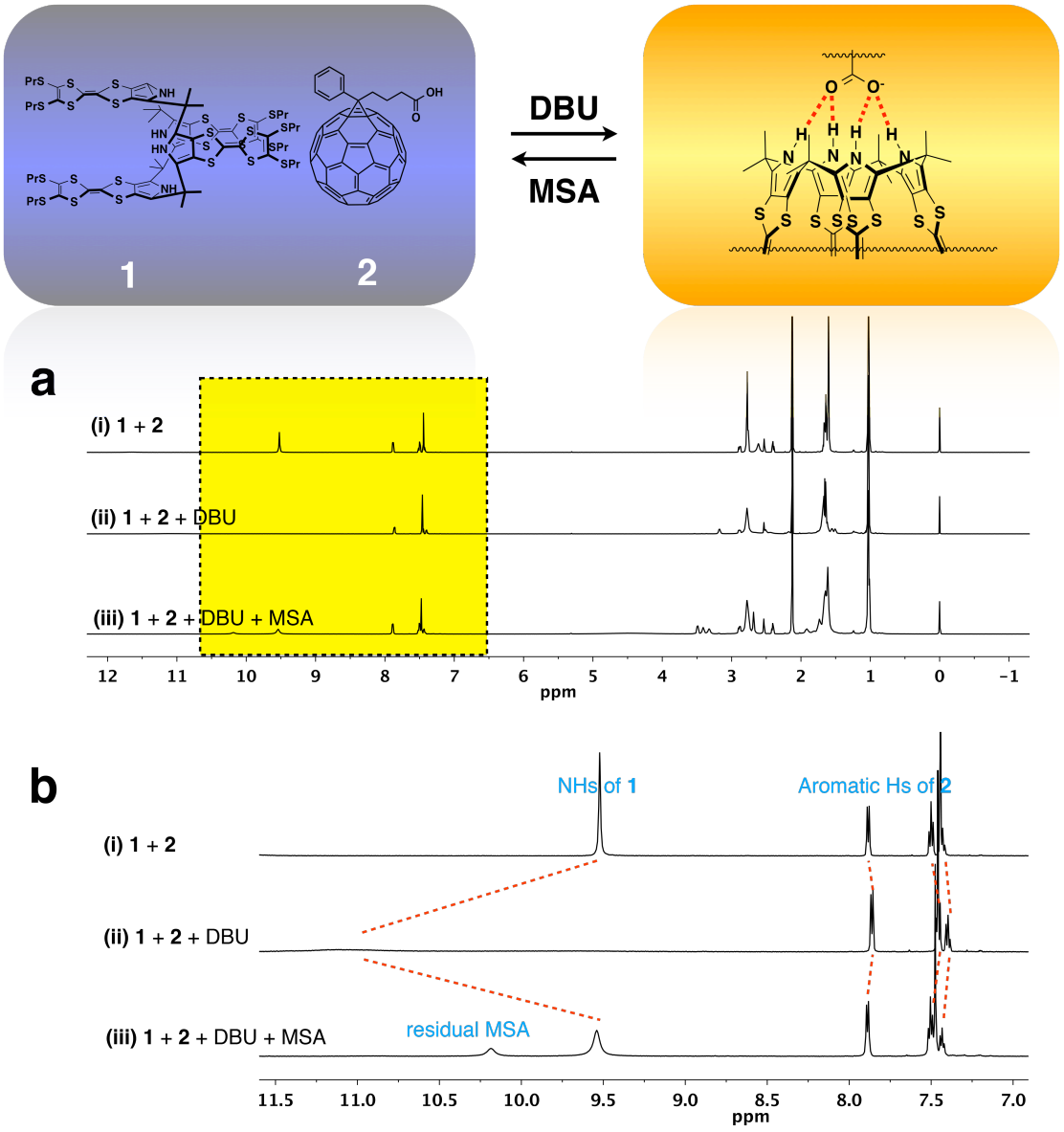

Figure S1. (a) Full-scale ^{1}H NMR spectra of (i) an equimolar mixture of **1** and **2** (2 mM each), (ii) the mixture of (i) with 3 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and (iii) the mixture of (ii) upon addition of 3 equiv of methanesulfonic acid (MSA) in the solvent system described in the Materials and Methods section. (b) Partial views of these same ^{1}H NMR spectra highlighting the signals for the NH protons of **1** and the aromatic protons of **2** and the changes observed upon sequential addition of DBU and MSA.

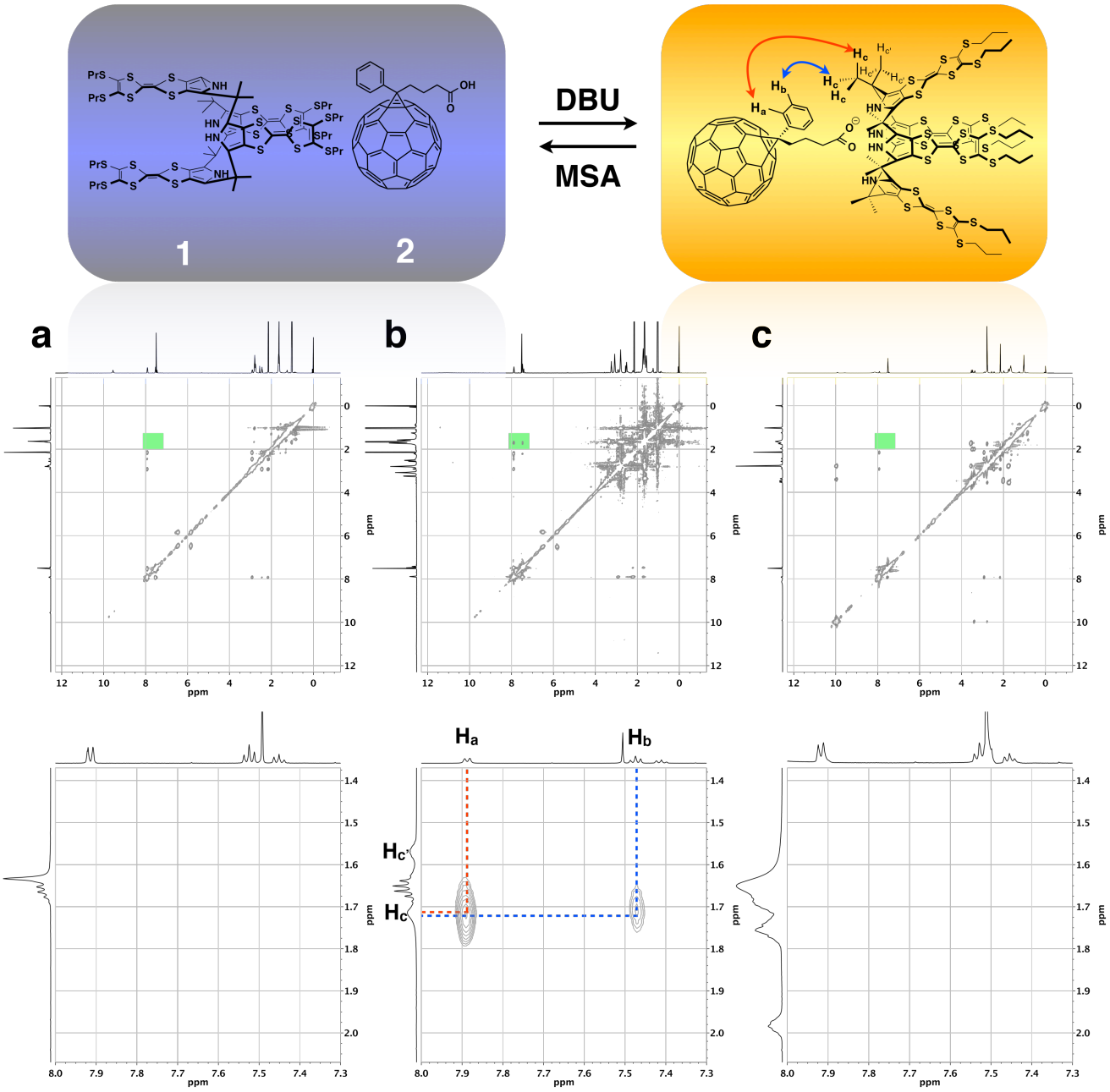

Figure S2. Full (top) and expanded (bottom) view of the 2D ^{1}H ROESY NMR spectra of (a) **1** + **2** (2 mM each), (b) **1** + **2** + 3.0 molar equiv of DBU, and (c) the spectra shown in (b) + 3.0 equiv of MSA. All spectra were recorded in the solvent system described in the Materials and Methods section.

Evidence that the addition of tetrabutylammonium fluoride, a source of a highly competitive anion, could be used to promote disassembly of the self-assembled structure came from diffusion ordered NMR spectroscopic analyses. In particular, the diffusion coefficients of proton signals corresponding to thiopropyl group in **1** increase from 1.45×10^{-9} m^2/s to 1.65×10^{-9} m^2/s (Figure S3).

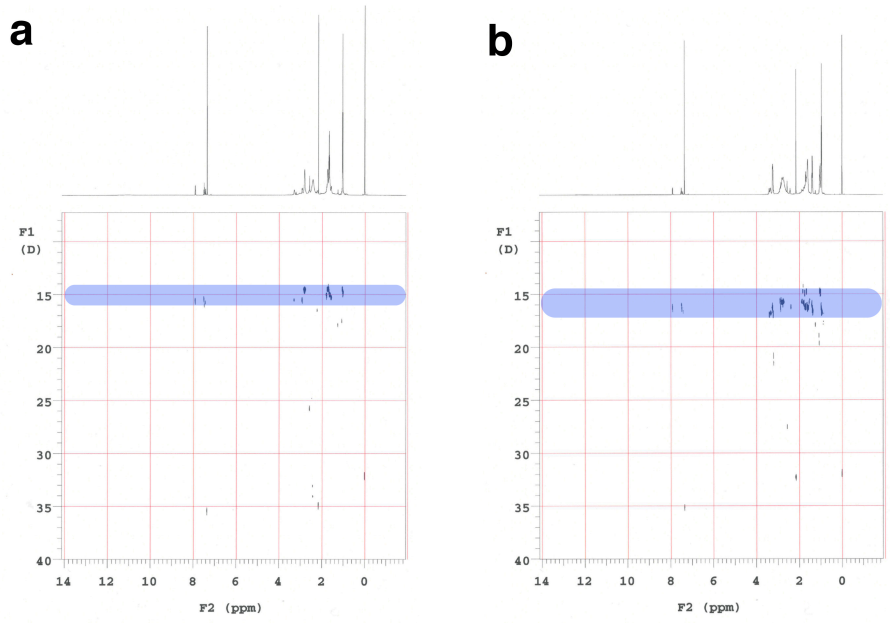

Figure S3. 2D ^{1}H DOSY NMR spectra of solutions containing **1** and **2** (2 mM each) recorded in the presence of (a) DBU (1.5 equiv) and (b) DBU (1.5 equiv) and TBAF (3 equiv). All spectra were recorded in the solvent system described in the Materials and Methods section.

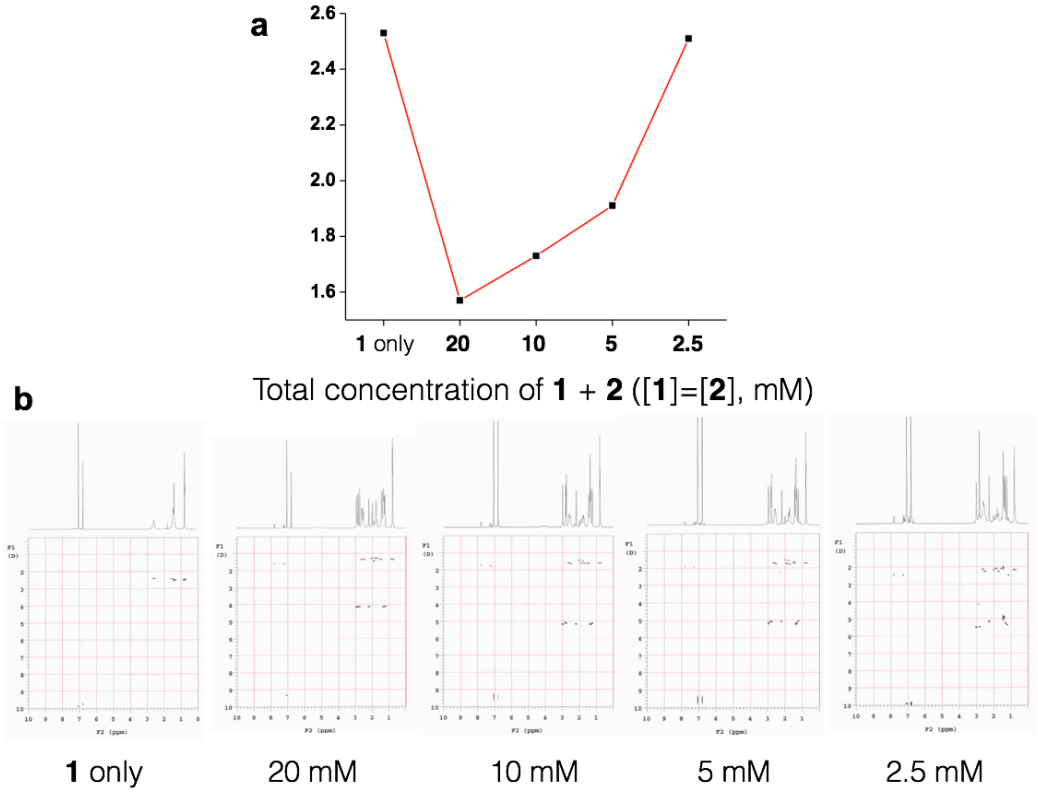

Figure S4. (a) Change in the diffusion coefficient D (plotted as Y-axis) as a function of concentration (X-axis) from ^{1}H DOSY NMR studies carried out in *o*-dichlorobenzene. The data points in (a) are the mean values of the diffusion coefficients recorded for the phenyl protons of **2** at each concentration where an analysis was made. (b) Spectra of an equimolar mixture of **1** and **2** recorded as a function of overall concentration in *o*-dichlorobenzene. Individual measurements were recorded upon diluting a solution of **1** + **2** wherein the initial concentration of the individual components, **1** and **2**, were each 10 mM. All samples were recorded in the presence of 3 molar equiv of DBU.

III. UV-Vis spectroscopic analyses and binding models

1. UV-Vis spectroscopic analyses

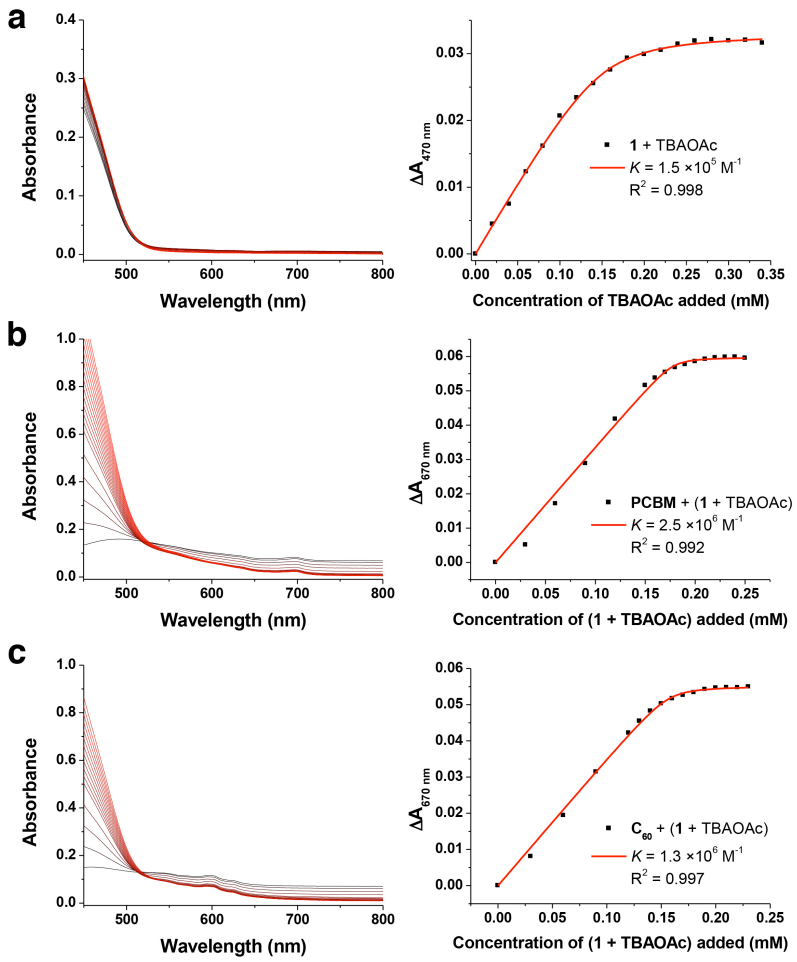

Figure S5. (a) Changes in the electronic spectrum of **1** (100 μM) seen upon the incremental addition of TBAOAc (tetrabutylammonium acetate) in the solvent system described in the Materials and Methods section (left) and the corresponding binding isotherm analysis (right). (b) Changes in the electronic spectrum of phenyl C_{61} butyric acid methyl ester (PCBM, 50 μM) seen upon the incremental addition of (**1** + TBAOAc) in the solvent system described in the Materials and Methods section (left) and the corresponding binding isotherm analysis (right). (c) Changes in the electronic spectrum of C_{60} (50 μM) seen upon the incremental addition of (**1** + TBAOAc) in the solvent system described in the Materials and Methods section (left) and the corresponding binding isotherm analysis (right).

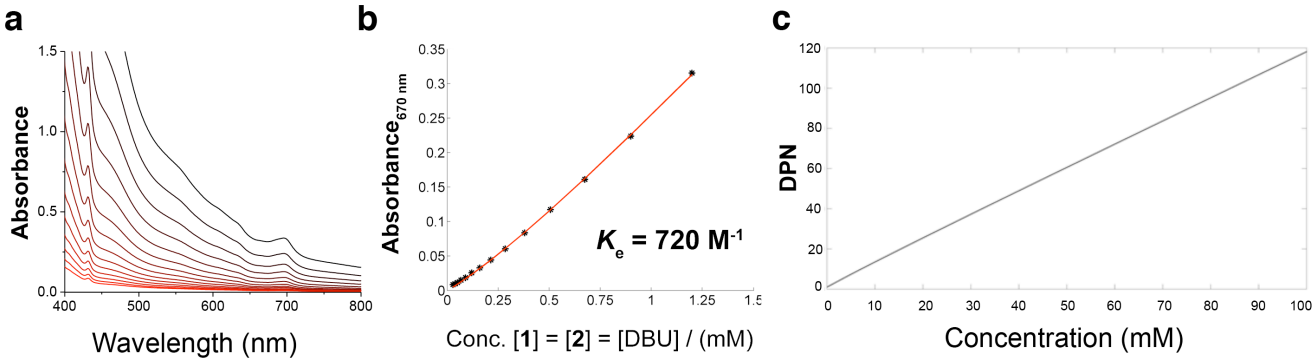

Figure S6. (a) Electronic spectra recorded upon sequential dilution of a solution containing equimolar quantities of **1**, **2**, and DBU in the solvent system described in the Materials and Methods section, (b) corresponding binding analysis, and (c) simulated plot showing the degree of polymerization.

2. Binding models and their analysis

i) Overall approach:

The association constant (K_a) for the binding of (**2**+DBU) + **1** and the aggregation or equilibrium constant (K_e) for the aggregation of the complex (**2**+DBU)•**1** were obtained via a two-step process that builds on an approach outlined by Hamelin and Jullien.[5] The first step involved obtaining K_a from a simple 1:1 binding model using data from the titration of (**2**+DBU) with **1** (Figure 3A and Figure 3C). The resulting K_a was then used in fitting the data from the sequential dilution studies involving equimolar quantities of **1**, **2** and DBU (Figure S6) to an aggregation model from Hamelin and Jullien[5] to obtain K_e. In both cases, a custom written Matlab program similar to one published previously[6] was used to perform a global analysis of the UV-Vis data in the region between 550-800 nm.

ii) Obtaining K_a:

The data from the titration of (**2**+DBU) with **1** was fitted to a simple 1:1 binding model to obtain K_a according to equations (S1) and (S2) using a custom written non-linear regression Matlab program[7] slightly modified from earlier work.[6]

$$[HG] = \left(\frac{1}{2} \left\{ \left([G]_0 + [H]_0 + \frac{1}{K_a} \right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a} \right)^2 + 4[H]_0[G]_0} \right\} \right) \qquad \text{(S1)}$$

$$A = \varepsilon_H([H]_0 - [HG]) + \varepsilon_{HG}([HG]) \quad \text{(S2)}$$

where [HG] = concentration of 1:1 host-guest complex, $[H]_0$ and $[G]_0$ the total (initial) concentration of the host and guest, respectively, K_a = (1:1) association constant, A = absorbance, ε_H = molar absorptivity of the free host and ε_{HG} = molar absorptivity of the 1:1 host-guest complex.

iii) Obtaining K_e:

The approach used here is based on the work by Hamelin and Jullien[5] and starts by defining the following two equilibria according to equations (S3) and (S4):

$$K_a = \frac{[HG]}{[H][G]} \quad \text{(S3)}$$

$$K_e = \frac{[(HG)_{j+1}]}{[HG][(HG)_j]} \quad \text{(S4)}$$

Here K_e = aggregation or equilibrium constant, $[HG]_j$ = concentration of the aggregated complex HG with degree of polymerization = j.

From these two equations Hamelin and Jullien[5] showed that if the concentrations of the host and guest are equal ($[H]_0 = [G]_0$), as is the case in the sequential dilution study shown in Figure S5, the concentration of the free host [H] (equal to [G]) can be obtained from the quintic (5th order) equation (S5)[5]:

$$[H]^5\{(K_a)^2(K_e)^2\} - [H]^4\{(K_a)^2(K_e)^2[H]_0\} - [H]^3\{2K_aK_e[H]_0\} + [H]^2\{2K_aK_e[H]_0 + K_a\} + [H] - [H]_0 = 0 \quad \text{(S5)}$$

This equation could not be solved numerically without fixing K_a first and hence reducing the number of unknown parameters to one (K_e). As explained by Hamelin and Jullien[5] and mentioned in the main text of this paper, the assumption that K_a can be estimated from the titration of H with G (here **2**+DBU with **1**) is valid provided $K_e < K_a$, as is the case here.

The K_a value obtained earlier (K_a = 1722 M^{-1} – Figure 3C) was therefore used in fitting the experimental data to the binding model based on equation (S5). The non-linear regression process starts by using an initial guess for the K_e and the K_a value above. These are then passed to the subroutine *fivedeg* in Matlab that was written to solve this quintic equation using the *roots* function:

```
function b=fivedeg(Ltot,htot,K11,K12);

% b = output of function = [H]
%Ltot and htot = Total conc of host and guest. K11 = Ka and K12 = Ke.

r = size(Ltot,1);%determines the number of datapoints
uu = ones(r,1);%creates a vector full of ones (1) of the same length as data
%this is done to reserve memory and speed up calculation

%Next the quintic equation is populated:

a1 = (uu.*(K11.^2).*(K12.^2));
a2 = (uu.*(-K11.^2).*(K12.^2).*htot);
a3 = (uu.*((-2.*K11.*K12)));
a4 = (uu.*((2.*K11.*K12.*Ltot)+K11));
a5 = (uu.*(1));
a6 = (uu.*(-htot));


a = [a1 a2 a3 a4 a5 a6];

r = size(a,1);%determs the size of a

b = zeros(r,1);%creates a vector the size of r full of zeros (to reserve memory)

for n = 1:r; %starts a loop which solves the quintic equation row by row
   x = roots(a(n,:));%for each row, x = the five solutions of the quintic equation
   tt=real(x(5));

% as it turns out, roots always returns last the smallest real solution given the
%conditions used here.

   b(n) = tt;
end %end of subprogram
```

The output of this function was then used to calculate [H] and from that, [HG] as [HG] = $[H]_0$-[H]. The absorbance (A) was then calculated according to equation (S2) above from [H] and [HG] using the left hand matrix division (linear regression) function in Matlab. Iteration using the Simplex algorithm (*fminsearch* in Matlab) then yielded K_e = 720 M^{-1} after converging to the set level of tolerance ($<10^{-18}$).

iv) Obtaining DPN:

The degree of polymerization; DPN (Figure S5c) was obtained from a modified version of the Carother's equation (S6):

$$DPN = \frac{1}{1-p} \qquad \text{(S6)}$$

Here p = mole fraction of monomers that have polymerized. It follows in simple aggregating systems with equimolar concentration of the building blocks such as in the present case, that the mole fraction of the free (non-aggregated) species [H] $\alpha = [H]/[H]_0 = 1-p$. Hence, equation (S6) can be rearranged to give equation (S7):

$$\mathrm{DPN} = \frac{1}{1-p} = \frac{1}{\alpha} = \frac{[H]_0}{[H]} \qquad \text{(S7)}$$

When K_a, K_e, $[H]_0$ and $[G]_0$ are known, [H] can be calculated from equation (S5). DPN can thus be obtained from equation (S7) as shown in Figure S6c.

IV. Electrochemical analyses

SPr-TTF-C[4]P **1** is a teterapyrrolic macrocyclic compound that consists of four TTF-functionalized pyrroles **3**[3]. To optimize conditions under which **1** is fully oxidized to its octa-cationic species ($2e^-$ from each TTF unit × 4) without decomposition of the medium, the redox behavior of the known[3] monomer **3** (structure shown in Figure S7b) was also studied.

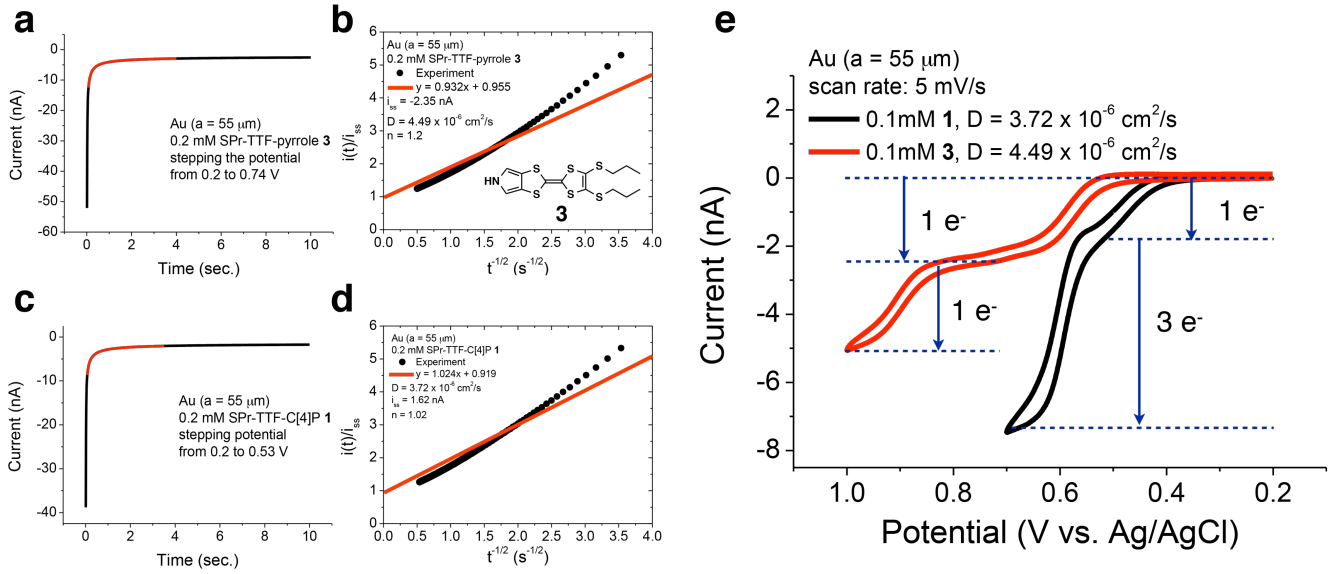

Figure S7. Chronoamperograms measured by stepping the potential (a) from 0.2 to 0.74 V for 10 s (black) for a 0.2 mM solution of **3**[3] (c) from 0.2 to 0.53 V in 0.2 mM of **1** in the solvent system described in the Materials and Methods section. (b) and (d) plot of $i(t)/i_{ss}$ vs. $t^{-1/2}$ obtained from the current region marked with a red line in panels (a) and (c), respectively. (e) Cyclic voltammograms (CVs) measured in 0.1 mM of **1** (black) and the same concentration of **3** (red) on a Au UME with radius of 55 μm at 5 mV/s, respectively. All experiments were performed in the solvent mixtrue described in the Materials and Methods section but containing 0.1 M tetrahexylammonium tetrafluoroborate ($THABF_4$) as a supporting electrolyte.

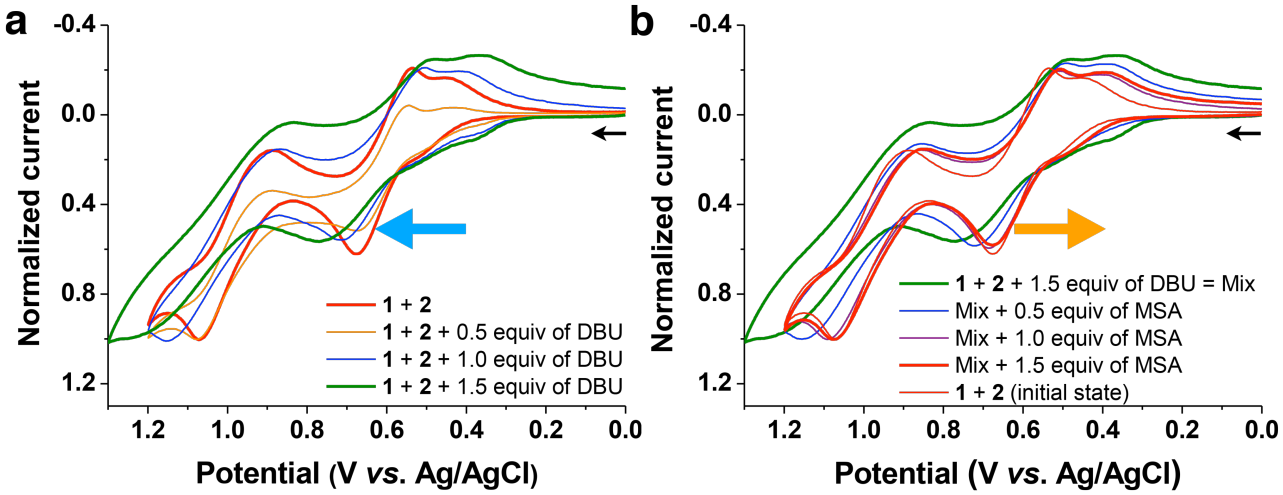

Figure S8. Full view of cyclic voltammograms recorded upon the sequential addition of (a) DBU and (b) MSA to a mixture of **1** and **2** in the solvent system detailed in the Materials and Methods section but containing $THABF_4$ (0.1 M) as the supporting electrolyte. The measurements in question were performed with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode.

V. Dynamic light scattering (DLS) experiments

Table S1. Formation and deformation of oligomers by acid/base chemistry

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU	**Mean**	---	---	25	6.1E5	2.0	0	26	0.16	1.01
	S	---	---	0	1.5E5	1.1	0	32	0.07	0.01
	%S	---	---	0	24.1	55.5	---	122	43.5	1.13
	S²	---	---	0	2.2E10	1.3	0	1045	0.01	0
	Min	---	---	25	4.0E5	0.0	0	0	0	1
	Max	---	---	25	9.3E5	4.9	0	136	0.36	1.04

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P	**Mean**	---	---	25	6.5E6	52.5	0	51400	0.08	1.04
	S	---	---	0	1.0E6	29.0	0	54300	0.02	0.02
	%S	---	---	0	16.0	55.2	103.3	105	30.75	1.56
	S²	---	---	0	1.1E12	838.7	0	2.94E9	0.001	0
	Min	---	---	25	5.0E5	0.0	0	0	0	1
	Max	---	---	25	8.3E6	108.6	0.1	195000	0.11	1.07

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P + MSA	**Mean**	---	---	25	8.9E6	19.4	16.1	11300	0.04	1.02
	S	---	---	0	1.9E6	22.9	17.1	19500	0.02	0.01
	%S	---	---	0	21.5	118.2	106.7	173	41.74	1.26
	S²	---	---	0	3.6E12	525.2	293.1	3.81E8	0	0
	Min	---	---	25	5.1E6	0.0	0	0	0	1
	Max	---	---	25	1.3E7	73.4	48.2	78100	0.08	1.05

Table S2. Concentration dependent studies; the total concentration refers to [**1**] + [**2**].

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P Total concentration 20 mM	**Mean**	---	---	25	1.4E6	198.3	13	1.11E7	0.56	1.08
	S	---	---	0	2.6E6	483.3	12.8	4.18E7	0.20	0.12
	%S	---	---	0	1.9	243.7	98.2	377	35.02	10.66
	S²	---	---	0	6.5E10	2.3E5	162.7	1.75E15	0.038	0.013
	Min	---	---	25	1.1E6	24.9	0	6240	0.40	0.94
	Max	---	---	25	2.3E6	2037.1	23.8	1.86E8	1.06	1.48

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P Total concentration 10 mM	**Mean**	---	---	25	6.1E5	82.3	6.9	6.2E5	0.4	1.04
	S	---	---	0	6.2E4	131.1	12	2.2E6	0.20	0.07
	%S	---	---	0	10	159.3	166	360	46.8	7.01
	S²	---	---	0	3.9E9	17185.4	131	4.9E12	0.03	0.005
	Min	---	---	25	5.4E5	29.3	0	9.1E3	0.3	1.00
	Max	---	---	25	8.2E5	584.6	36	1.0E7	1.0	1.30

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P Total concentration 5 mM	**Mean**	---	---	25	6.5E5	55.5	3.3	4.3E4	0.3	1.01
	S	---	---	0	8.5E4	10.8	8.2	2.3E4	0.02	0.02
	%S	---	---	0	13	19.5	246.2	55	8.1	2.14
	S²	---	---	0	7.3E9	116.6	66.5	5.4E8	0	0
	Min	---	---	25	5.3E5	48.1	0	2.9E4	0.3	1.0
	Max	---	---	25	9.1E5	84.1	23.8	1.1E5	0.3	1.07

		Item	Time (s)	Temp (C)	Intensity (Cnt/s)	Radius (nm)	%Pd	Mw-R (kDa)	Amp	Baseline
PCBA + DBU + TTF-C[4]P Total concentration 4 mM	**Mean**	---	---	25	6.5E6	52.5	0	5.1E4	0.07	1.03
	S	---	---	0	1.0E6	29.0	0	5.4E4	0.02	0.01
	%S	---	---	0	15	55.2	103.3	1.1E2	30.76	1.56
	S²	---	---	0	1.1E12	838.7	0	3.0E9	0.001	0
	Min	---	---	25	5.0E6	0.0	0	0	0	1
	Max	---	---	25	8.4E6	108.6	0.1	2.0E5	0.11	1.07

- [**1**] = [**2**]

- Note: TTF-C[4]P and PCBA refer to compounds **1** and **2**, respectively.
- Solvent: *o*-dichlorobenzene

Table S3. Mean value from four DLS measurements for the formation and deformation of oligomers by acid/base chemistry (Figure 4A).

Conditions	Mean Value (nm)	Error (nm)
2 + DBU	2.5	0.5
2 + DBU + **1**	47.4	5.2
2 + DBU + **1** + MSA	13.4	6.1

Table S4. Mean value from four DLS measurements for concentration dependent studies (Figure 4B).

Total concentration ([1]=[2], mM)	Mean Value (nm)	Error (nm)
4	47.4	5.2
5	59.1	8.0
10	92.8	10.5
20	179.8	21.6

VI. References

(1) Nielsen, K. A.; Cho, W. -S.; Jeppesen, J. O.; Lynch, V. M.; Becher, J.; Sessler, J. L. *J. Am. Chem. Soc.* **2004**, *126*, 16296–16297.

(2) Hummelen, J. C.; Knight, B. W.; LePeg, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532–538.

(3) Jeppesen, J. O.; Takimiya, K.; Jensen, F.; Brimert, T.; Nielsen, K.; Thorup, N.; Becher, J. *J. Org. Chem.* **2000**, *65*, 5794-5805

(4) Denuault, G.; Mirkin, M. V.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *308*, 27–38.

(5) Hamelin, B.; Jullien, L. *J. Chem. Soc. Faraday Trans.* **1997**, *33*, 2153–2160.

(6) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

(7) www.supramolecular.org