Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary information

for

Solvent-induced switching between two supramolecular assemblies of a guanosine-terthiophene conjugate

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Preparation of samples for spectroscopic measurements

Chloroform solutions of **1**-Kpic. To 1 mL of a 15 mM solution of **1** in $CHCl_3$ (or $CDCl_3$) were added 210 μL of a 8.8 mM ACN (or ACN-d_3) solution of K-picrate (0.125 eq of Kpic). The resulting solution was stirred for 20 min at room temperature and, when necessary, it was diluted up to 3, 0.3 or 0.03 mM with $CHCl_3$ (or $CDCl_3$).

Acetonitrile/chloroform 9/1 solutions of **1**-Kpic. In a typical experiment, 0.1 mL of a 3 mM chloroform solution of **1**-Kpic (prepared as described above) were added with 0.9 mL of ACN (or ACN-d_3) to give a 0.3 mM solution. When necessary, the resulting solution was diluted with ACN or ACN-d_3 up to 0.03 mM. All spectra were recorded after keeping samples at room temperature for 20 min.

Acetonitrile/chloroform 9/1 solutions of **1**. In a typical experiment, 0.1 mL of a 3 mM solution of **1** in $CHCl_3$ (or $CDCl_3$) were added with 0.9 mL of ACN (or ACN-d_3) to give a 0.3 mM solution. When necessary, this latter solution was diluted again (with ACN or ACN-d_3) up to 0.03 mM. All spectra were recorded after keeping samples at room temperature for 20 min.

Figure S1. CD spectra recorded at r.t. on **1**-KPic in $CHCl_3$ at different concentrations: 3 mM (red trace, path length cell = 0.01 cm), 0.3 mM (blue trace, path length cell = 0.1 cm), 0.03 mM (gray trace, path length cell = 1 cm).

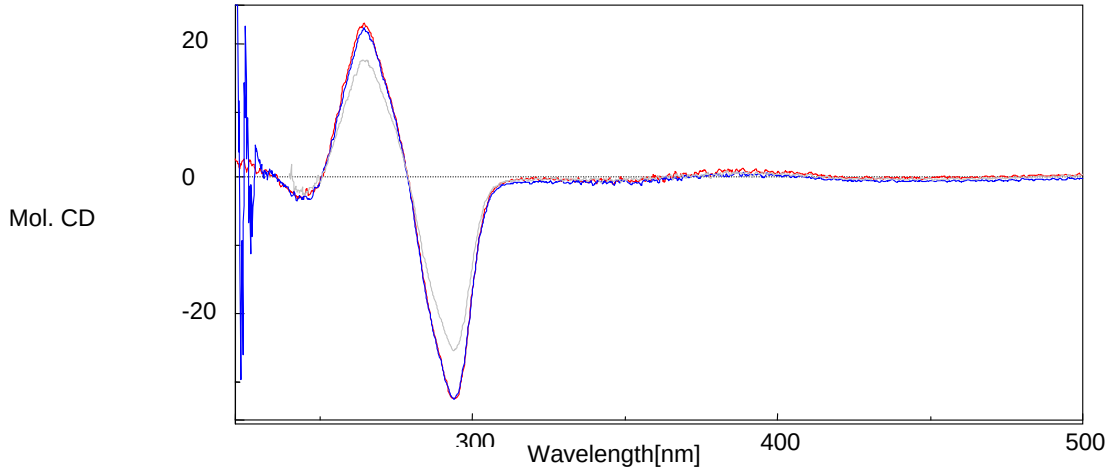


Figure S2. Comparison between CD/UV spectra recorded at r.t. on **1**-Kpicrate (pink trace) and **1**-Kformate (red trace) in $CHCl_3$ (c = 3 mM, path length cell = 0.01 cm).
The chloroform solution of **1**-KPic was prepared as described above (see experimental section).
The chloroform solution of **1**-KForm was prepared upon addition of 0.125 eq of solid K formate to a 3 mM chloroform solution of **1** and 48h of stirring at room temperature.

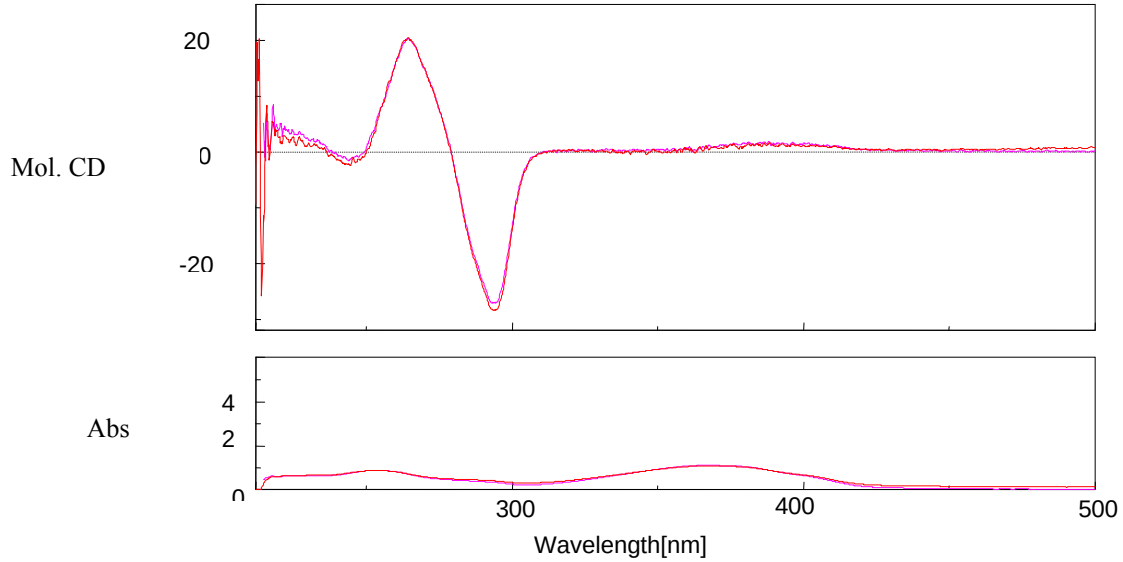


Figure S3. Comparison between ^{1}H NMR (600 MHz) spectra recorded at 25°C on **1**-KPicrate (a) and **1**-KFormate (b) in $CDCl_3$ (c = 3 mM).

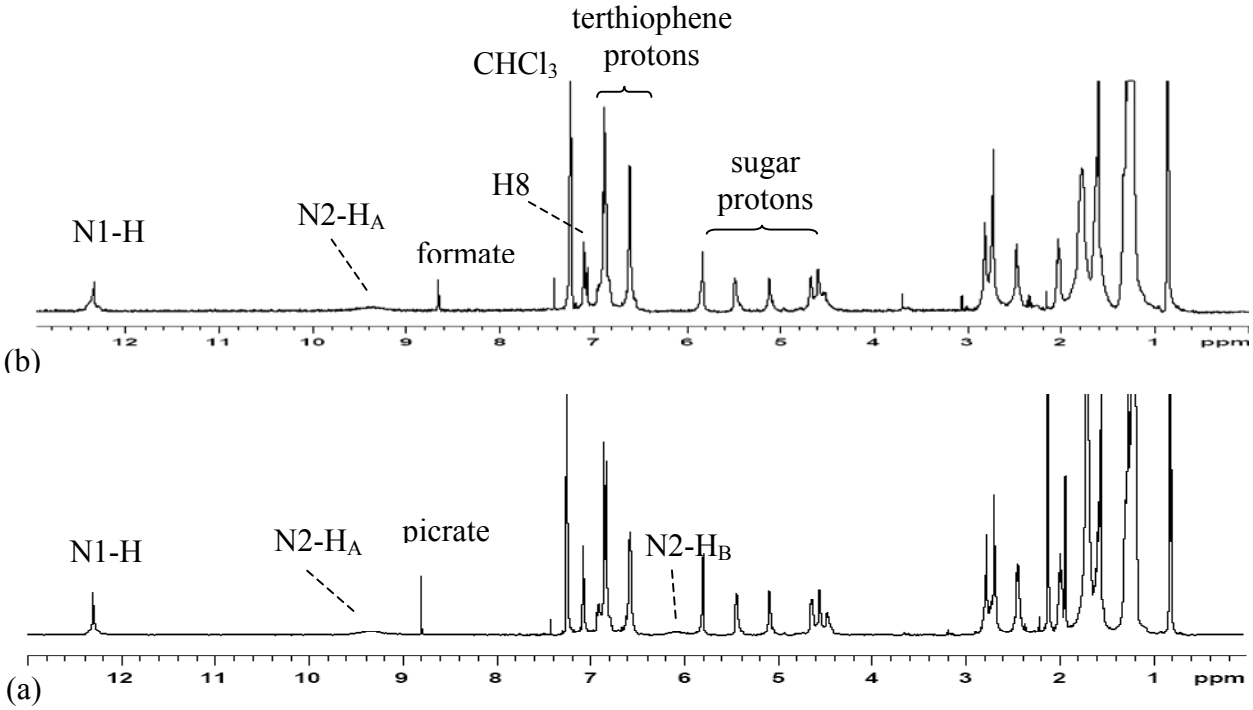


Figure S4. ^{1}H NMR (600 MHz) spectra recorded at 25°C on **1** in $CDCl_3$ at different concentrations (c = 0.3 mM (a); c = 15 mM (b)).

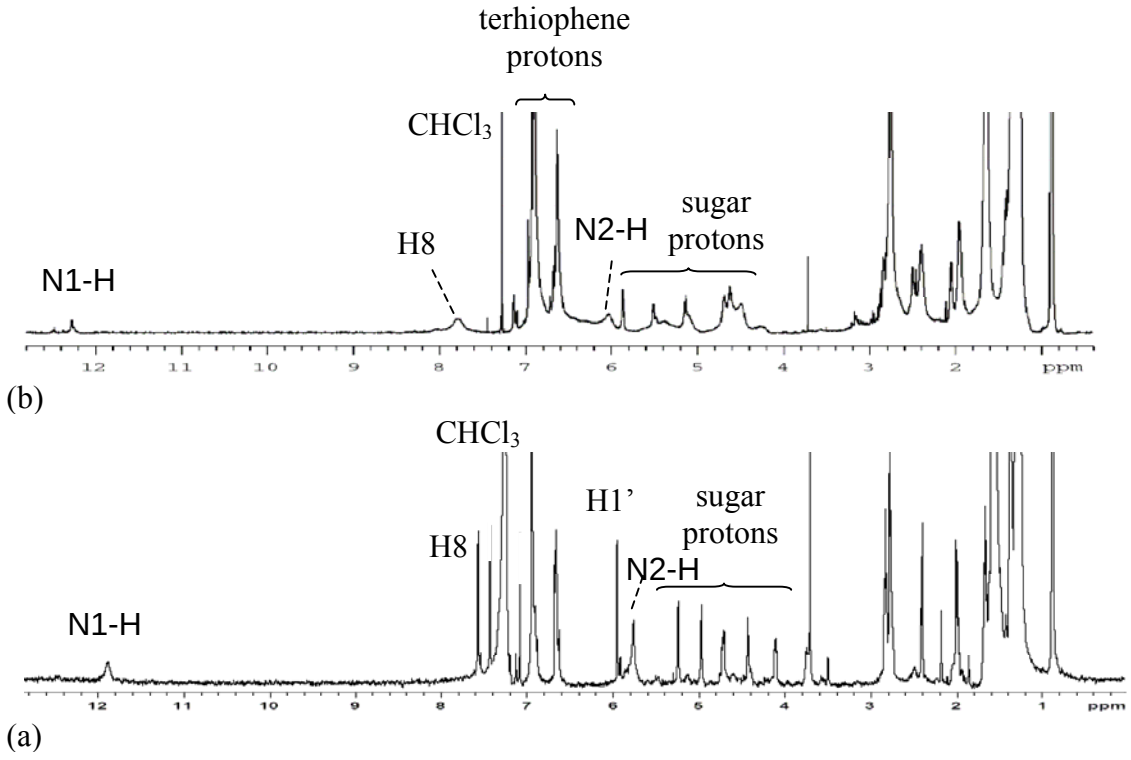
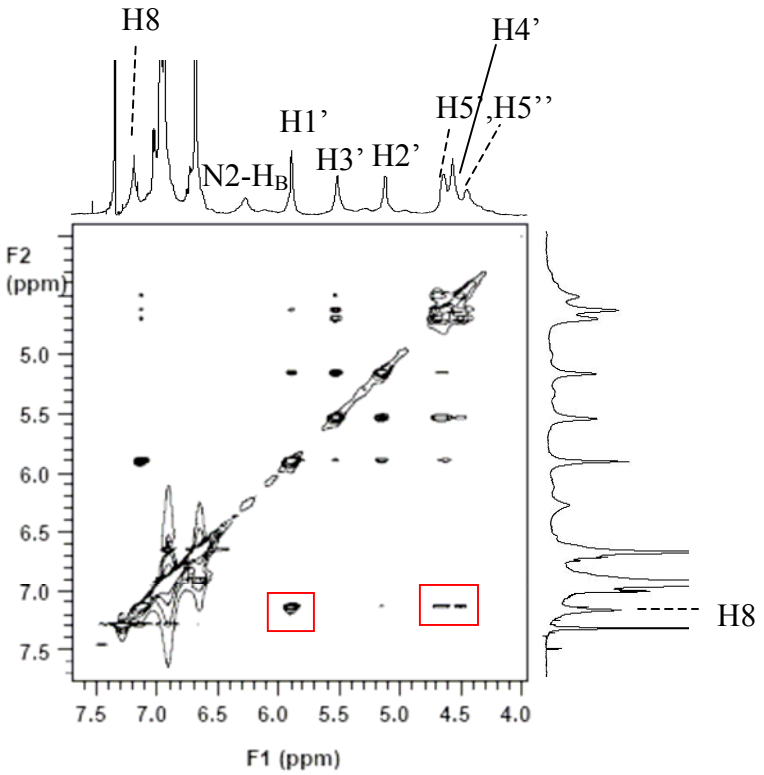


Figure S5. Portions of the NOESY spectrum (600 MHz, mixing time 200 ms) of **1**-KPic in $CDCl_3$ 15 mM recorded at –15°C. Relevant intermolecular cross-peaks for the D_4-octameric architecture (between H8 and H5'/H5'' (spectrum (a)), and between H8 and the two amino protons (spectrum (b)), are boxed in red lines. In spectrum (a) can be noted also the strong intramolecular NOE crosspeak between H8 and H1' indicative of a *syn* conformation around the glycosidic bond.

Spectrum (a)



Spectrum (b)

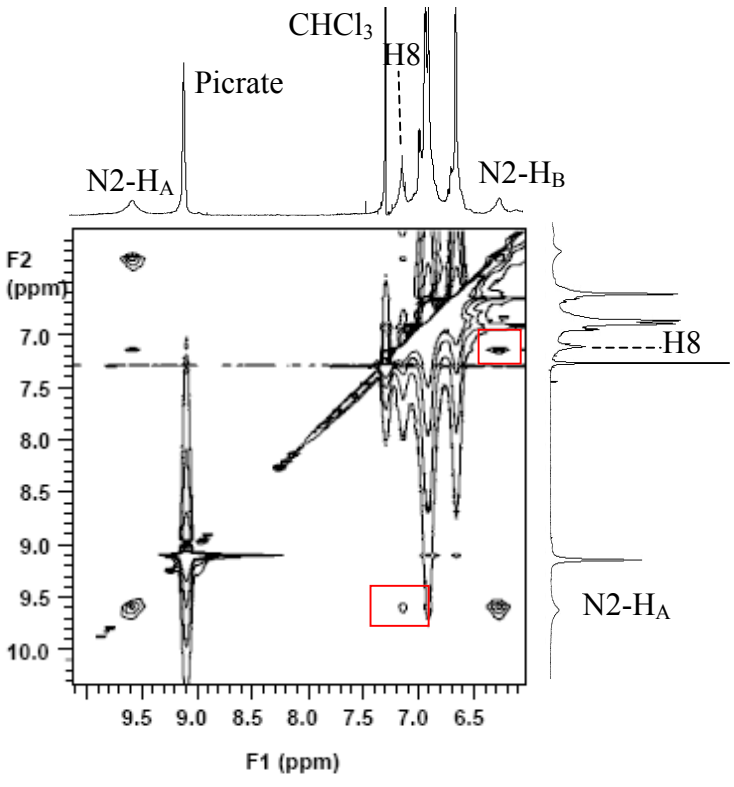


Figure S6. CD spectra recorded at r.t. on **1**-Kpic showing the partially reversible-switching between the two supramolecular chiral forms in the two different solvent conditions.
blue trace (cell path legth d = 0.1 cm): **1**-Kpic in ACN/$CHCl_3$ 9/1 0.3 mM is the initial solution S_i;
red trace (d = 1 cm): solution S_i diluted with ACN up to 0.03mM;
pink trace (d = 1 cm): solution S_i diluted with $CHCl_3$ up to 0.03 mM.
gray trace (d = 1 cm): freshly prepared solution of **1**-Kpic in $CHCl_3$ 0.03 mM.

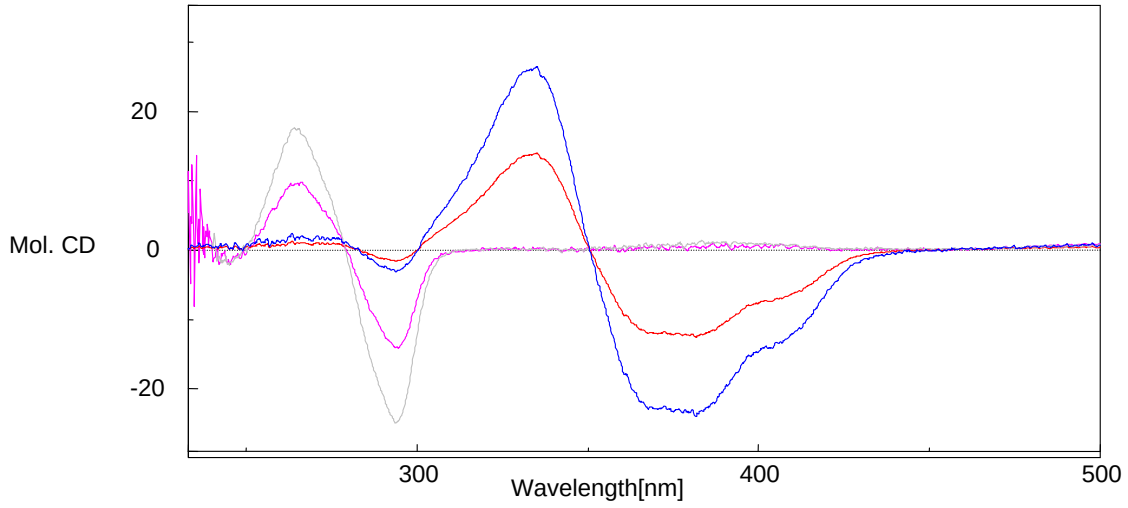


Figure S7. ^{1}H NMR (600 MHz) spectra of **1** in ACN/$CDCl_3$ 9/1 (c = 0.3 mM) recorded at 5°C (a) and 25°C (b).

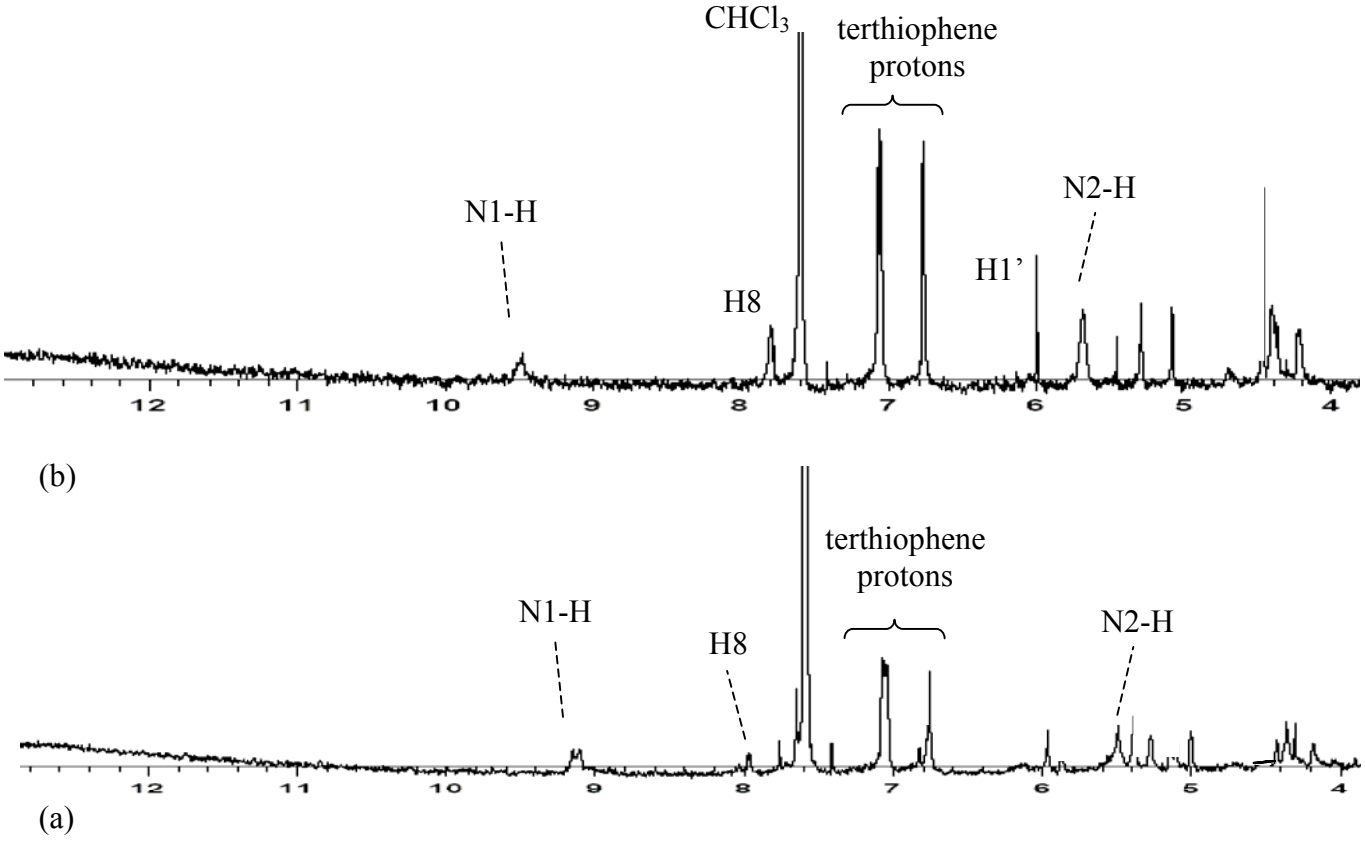
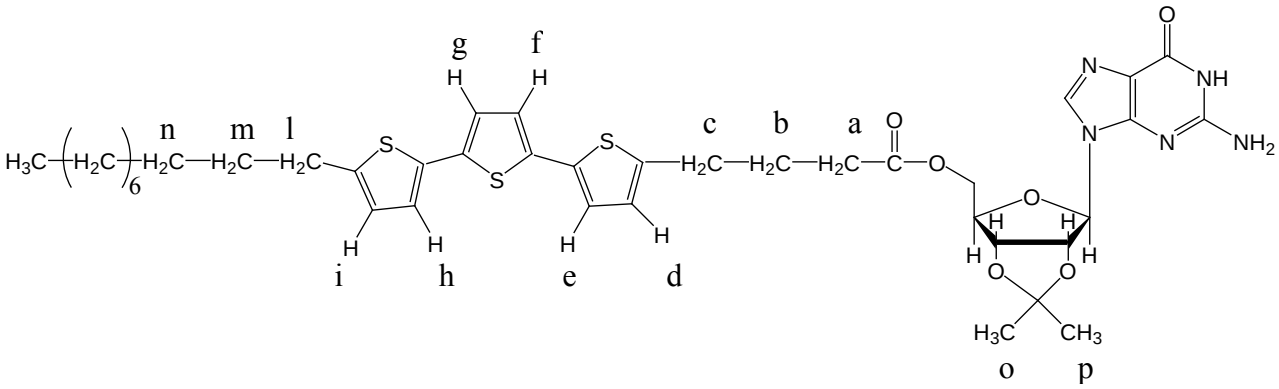
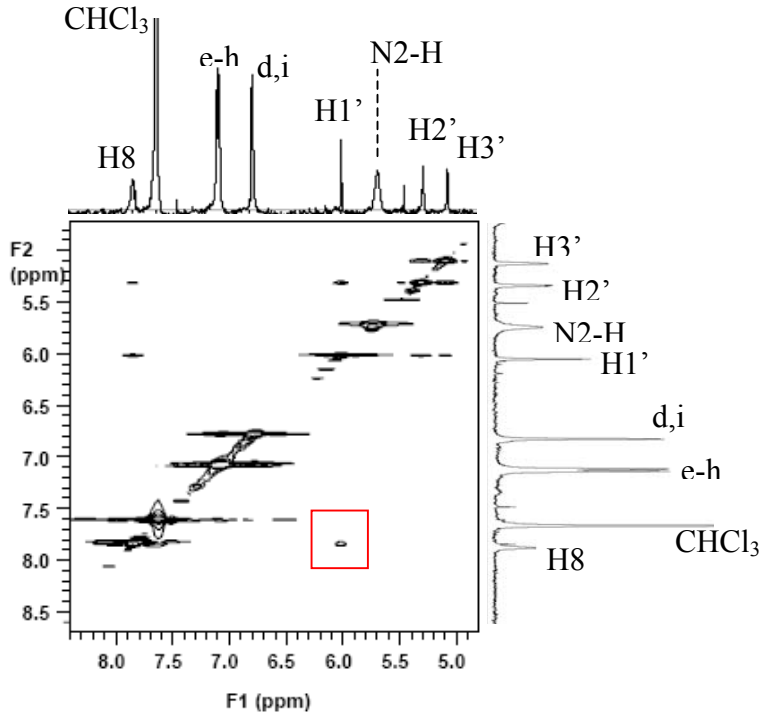
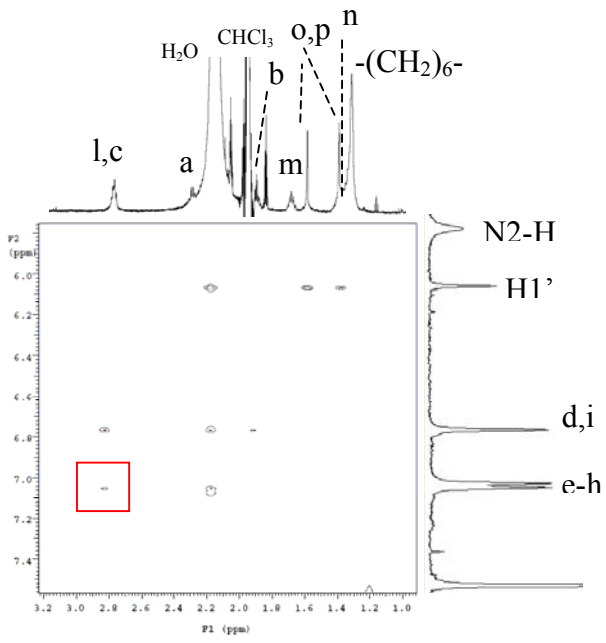


Figure S8. Portions of the NOESY spectrum (600 MHz, mixing time 200 ms) of **1** in $CD_3CN/CDCl_3$ 9/1 0.3 mM recorded at r.t. In spectrum (a) can be noted the intramolecular NOE crosspeak between H8 and H1' (stronger than between H8 and H2') indicative of a *syn* conformation around the glycosidic bond. In spectrum (b) NOE interactions between the terthiophene ring protons e-h and the methylene hydrogens c and l are observed. All signals have been assigned by COSY experiments.





spectrum (a)



spectrum (b)

Figure S9. CD/UV spectra recorded at r.t. on three different samples of **1**-Kpic in ACN/$CHCl_3$ 9/1 0.3 mM (cell path length = 0.1 cm) prepared according to the same experimental procedure.

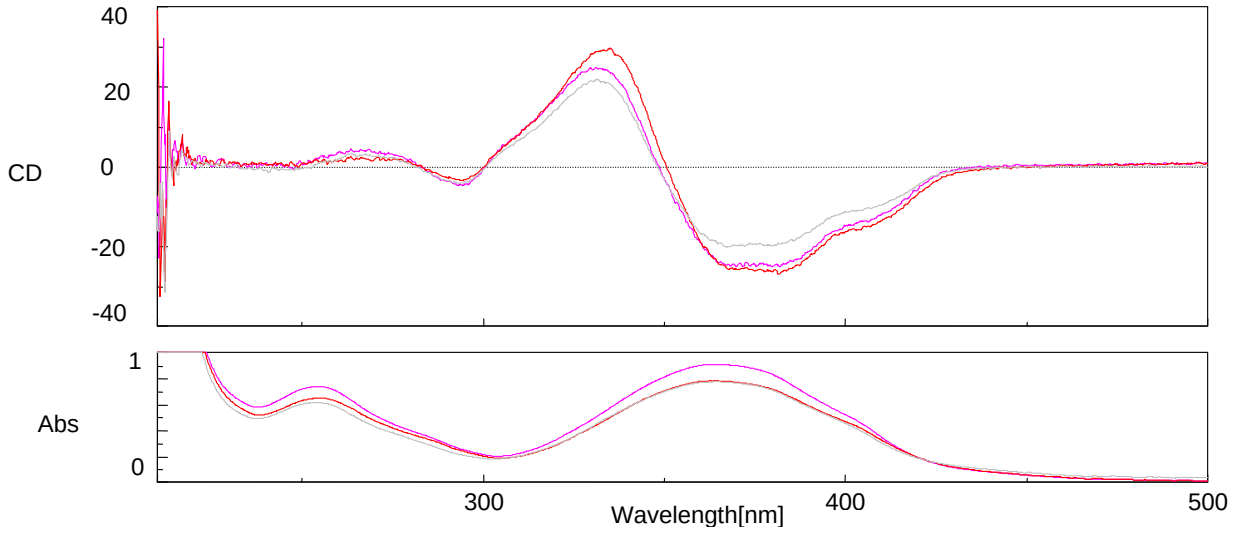


Figure S10. CD/UV spectra of **1**-Kpic in ACN/$CHCl_3$ 9/1 0.3 mM (cell path legth = 0.1 cm) recorded, at r.t., as a function of time: (a) freshly prepared solution (blue trace), (b) sample (a) after one night (red trace), (c) sample (a) after three days (gray trace), (d) sample (a) after four months (pink trace). The sample was stored in the fridge and each spectrum was recorded after 30 min of equilibration time at room temperature.

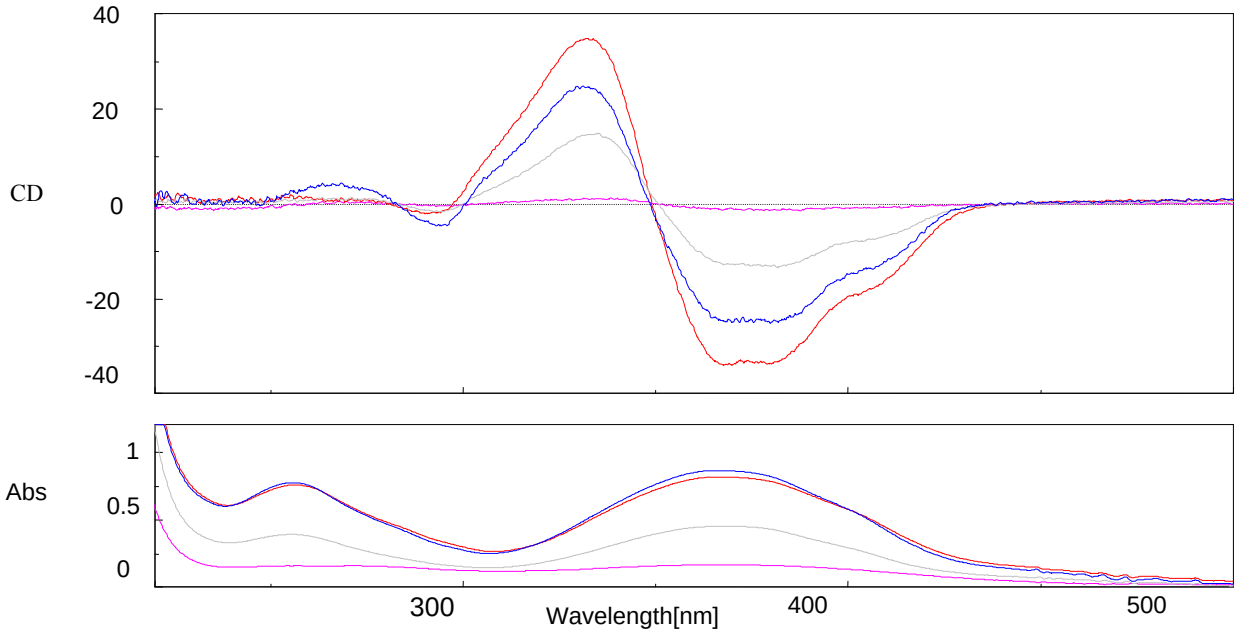


Figure S11. Dynamic Light Scattering measurement of **1**-KPic in ACN/$CHCl_3$ 9/1. Size distribution by intensity and undersize curve, D_H= 79.20 nm, PDI=0.05.

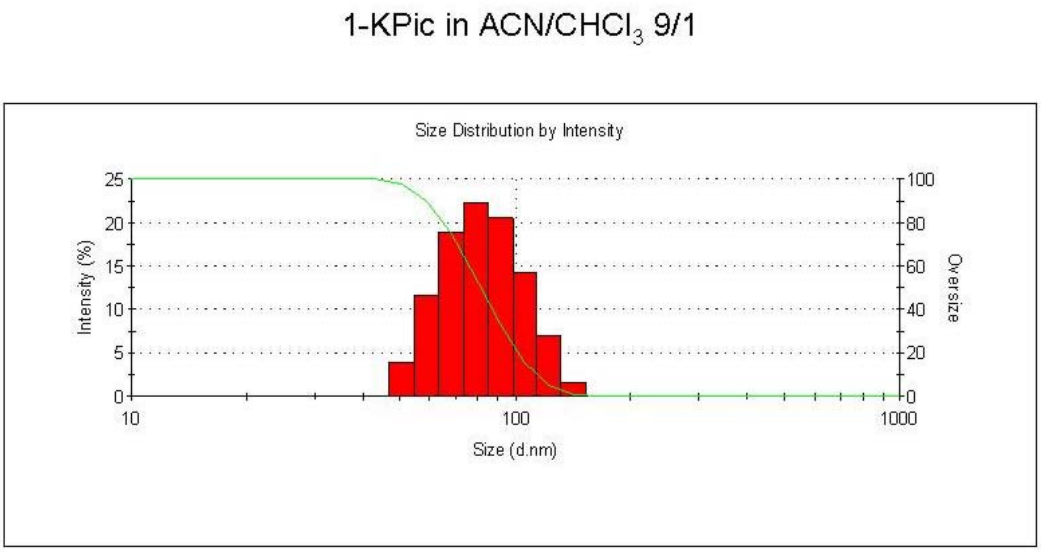


Figure S12. CD/UV spectra of **1**-Kpic in ACN/$CHCl_3$ 9/1 0.3 mM (cell path legth = 0.1 cm) recorded at variable temperature, (a) at 5°C (red trace), at 25°C (gray trace), at 40°C (blue trace), at 50°C (pink trace). All spectra were recorded after 20 min of equilibration time at each recording temperature.

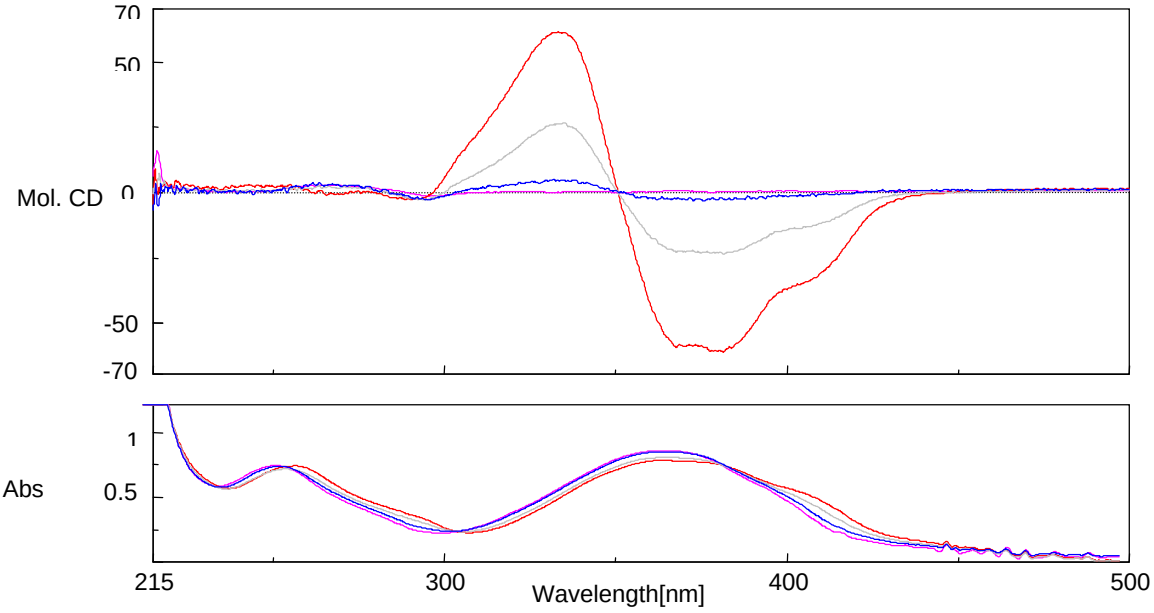
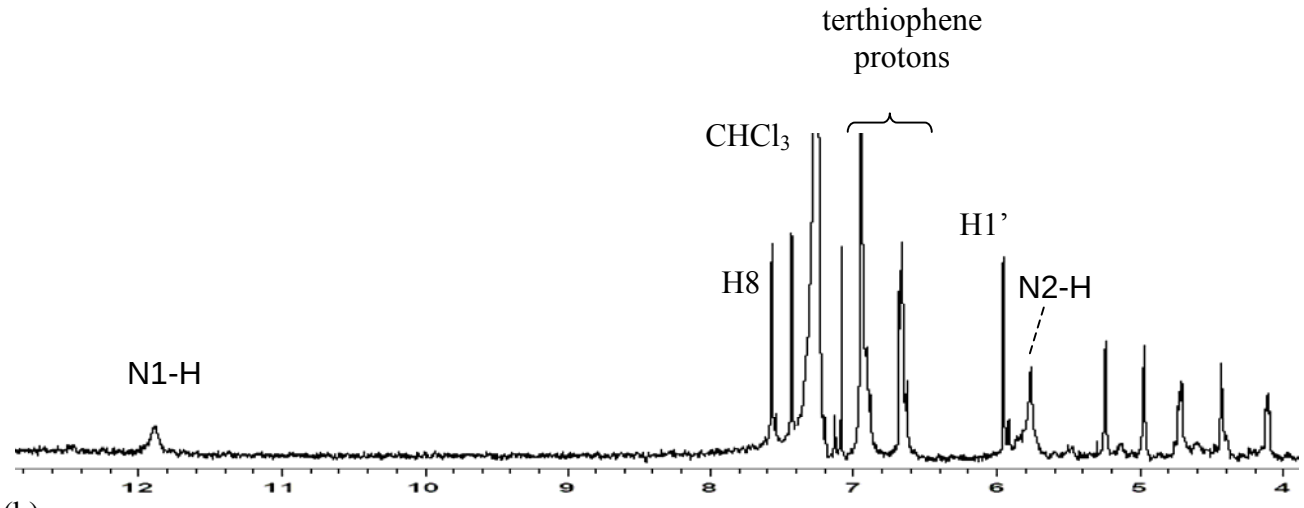
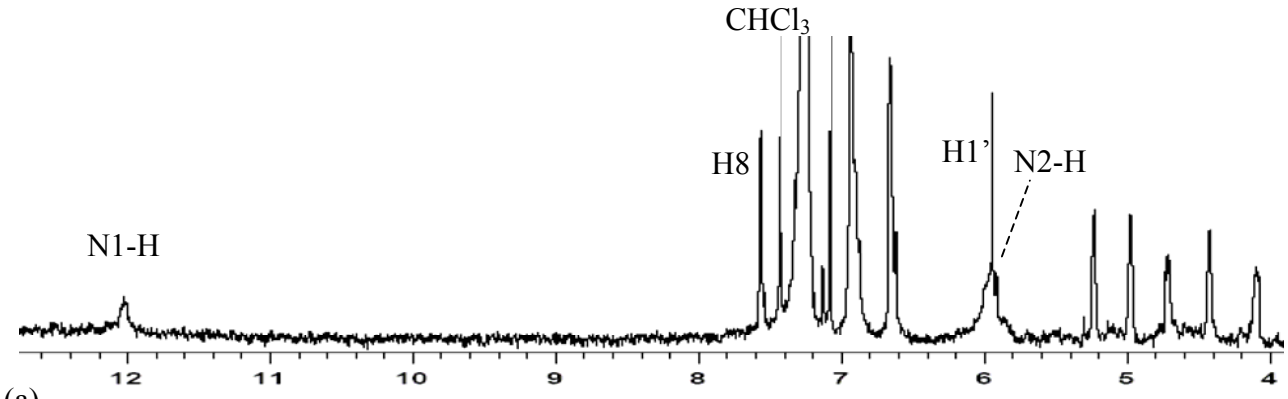


Figure S13. ^{1}H NMR (600 MHz) spectra of **1** in $CDCl_3$ (c = 0.3 mM) recorded at 5°C (a) and 25°C (b).



(b)



(a)