

Supporting Information for:

Playing supramolecular dominoes with light: Building and breaking a photoreversible G-quadruplex made from guanosine, boric acid and an azobenzene.

Silvia Pieraccini,^[a] Marilena Campitiello,^[a] Federica Carducci,^[b] Jeffery T. Davis,^{*[c]} Paolo Mariani,^{*[b]} and Stefano Masiero^{*[a]}

[a] Dipartimento di Chimica "Giacomo Ciamician" Università di Bologna, via San Giacomo 11 – 40126 Bologna (Italy)

[b] Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona (Italy)

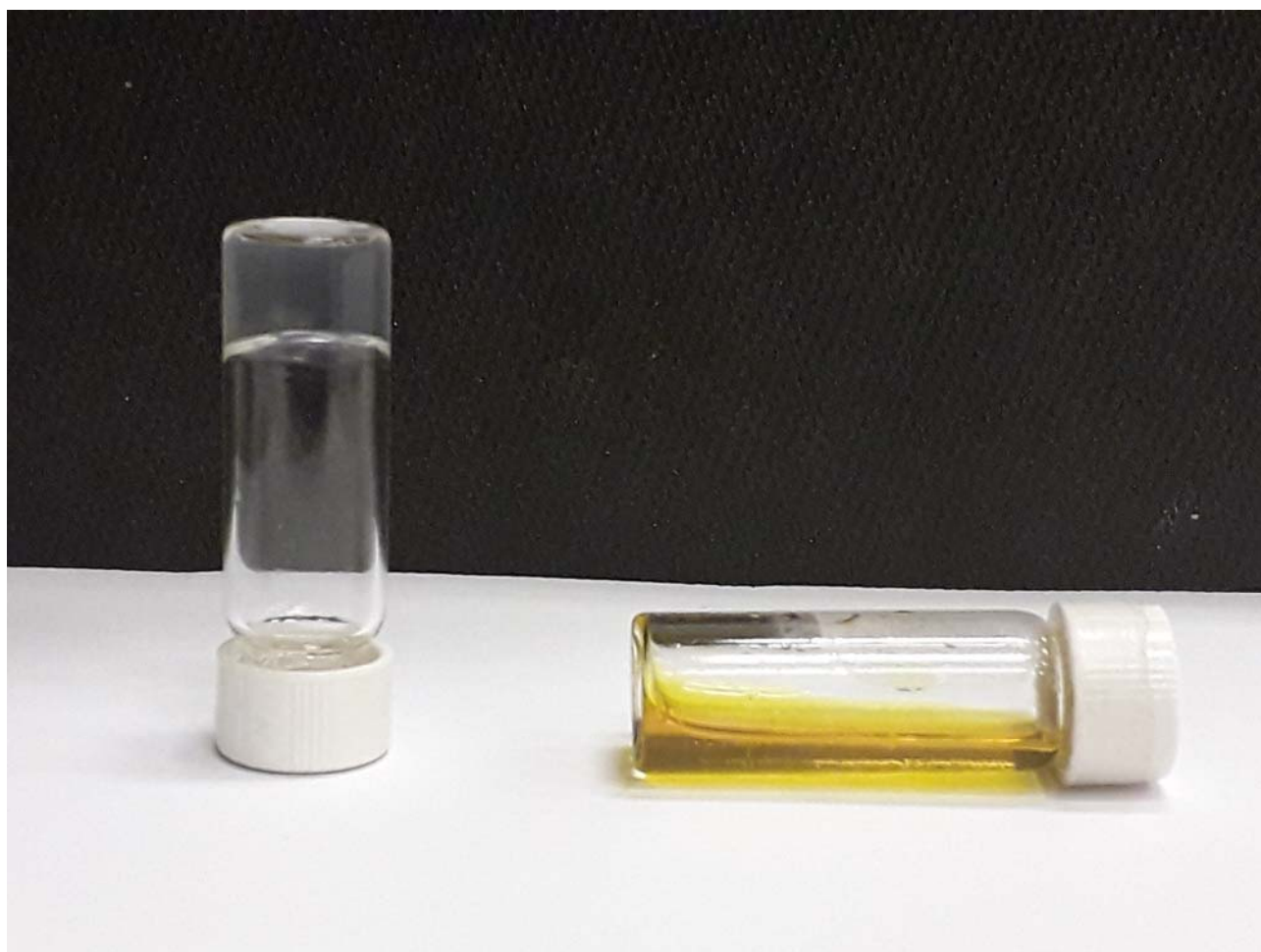
[c] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 USA

stefano.masiero@unibo.it

p.mariani@staff.univpm.it

jdavis@umd.edu

Table of contents	pag.
Pictures showing the effect of dye 1 on a GBK hydrogel	2
Variable temperature ¹ H NMR experiments performed on the GBK/ E-1 complex	3
NOEsy spectra performed on the KBK/ E-1 complex	4
CD spectra recorded on the GBK/ 1 and GBLi/ 1 solutions during photoisomerization of the dye	6
Comparison among CD spectra recorded on the GBK/ E-1 complex, an analogous sample prepared from inosine, 2'-dG and a GB solution added with E-1	6
Variable temperature CD experiments performed on the GBK/ E-1 complex	7
CD spectra recorded on GBK during titration with dye E-1	8
Variable temperature SAXS results from E-1 /GBK samples at different composition.	9
Estimated diameters of all possible G-quartets formed by GBK components	10



Picture S1. The disrupting effect of dye **1** on a GBK hydrogel. Left side: 30 mM GBK hydrogel; right side: 30 mM GBK hydrogel added with *E-1*, according to a [total-G]/[*E-1*] molar ratio = 4. Samples were prepared as reported in the experimental section, and pictures were taken half-an-hour after sample preparation.

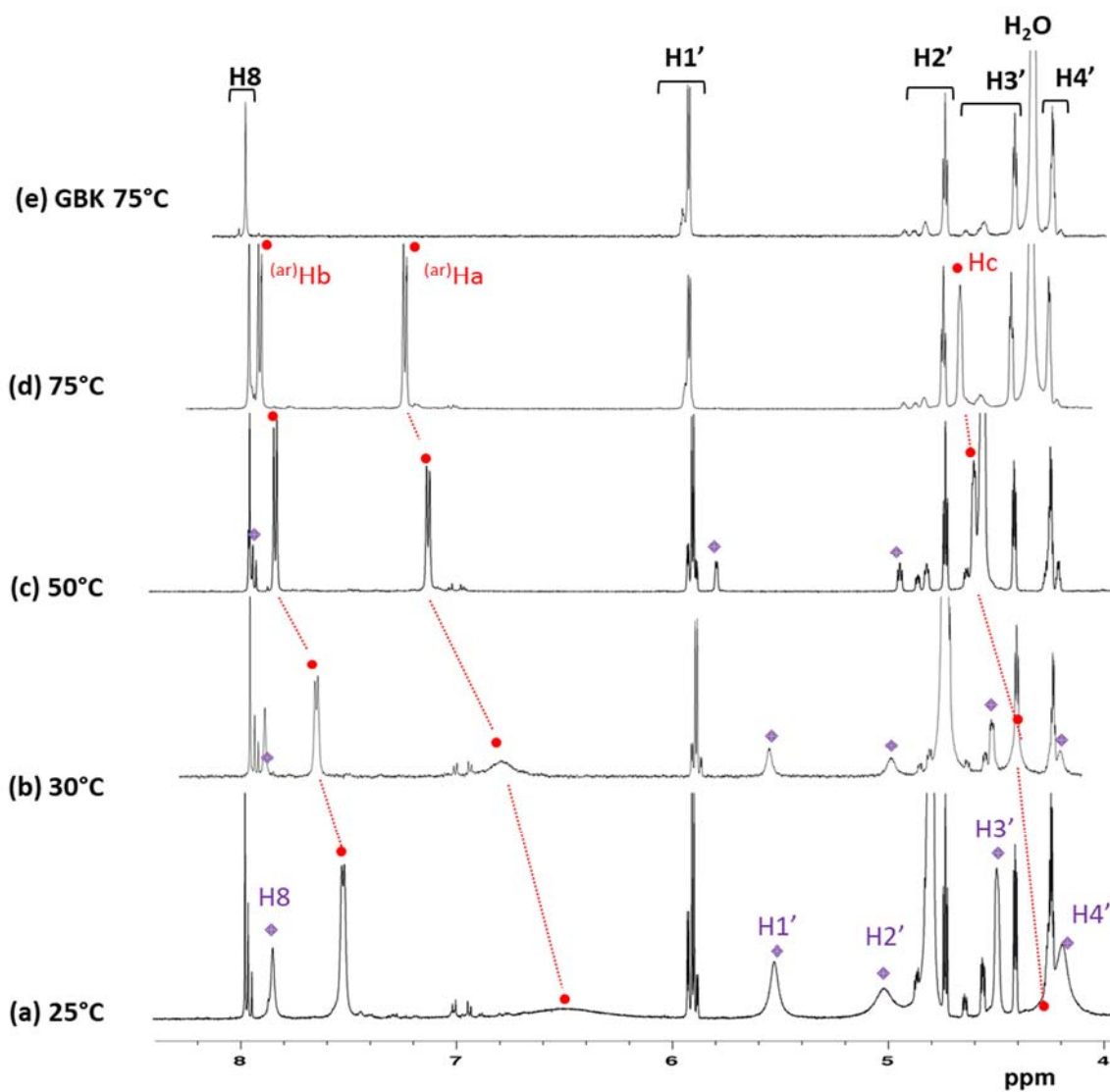


Figure S1. $(VT)^1\text{H}$ NMR spectra recorded in D_2O between 25 and 75°C on the 10 mM GBK solution added with *E-1* ($[\text{total-G}]/[\text{E-1}] = 3$). Proton signals corresponding to associated guanosines (purple rhombuses) and *E-1* (full red circles) are evidenced. ^1H NMR spectrum (e) recorded on 10 mM GBK at 75°C is reported for comparison.

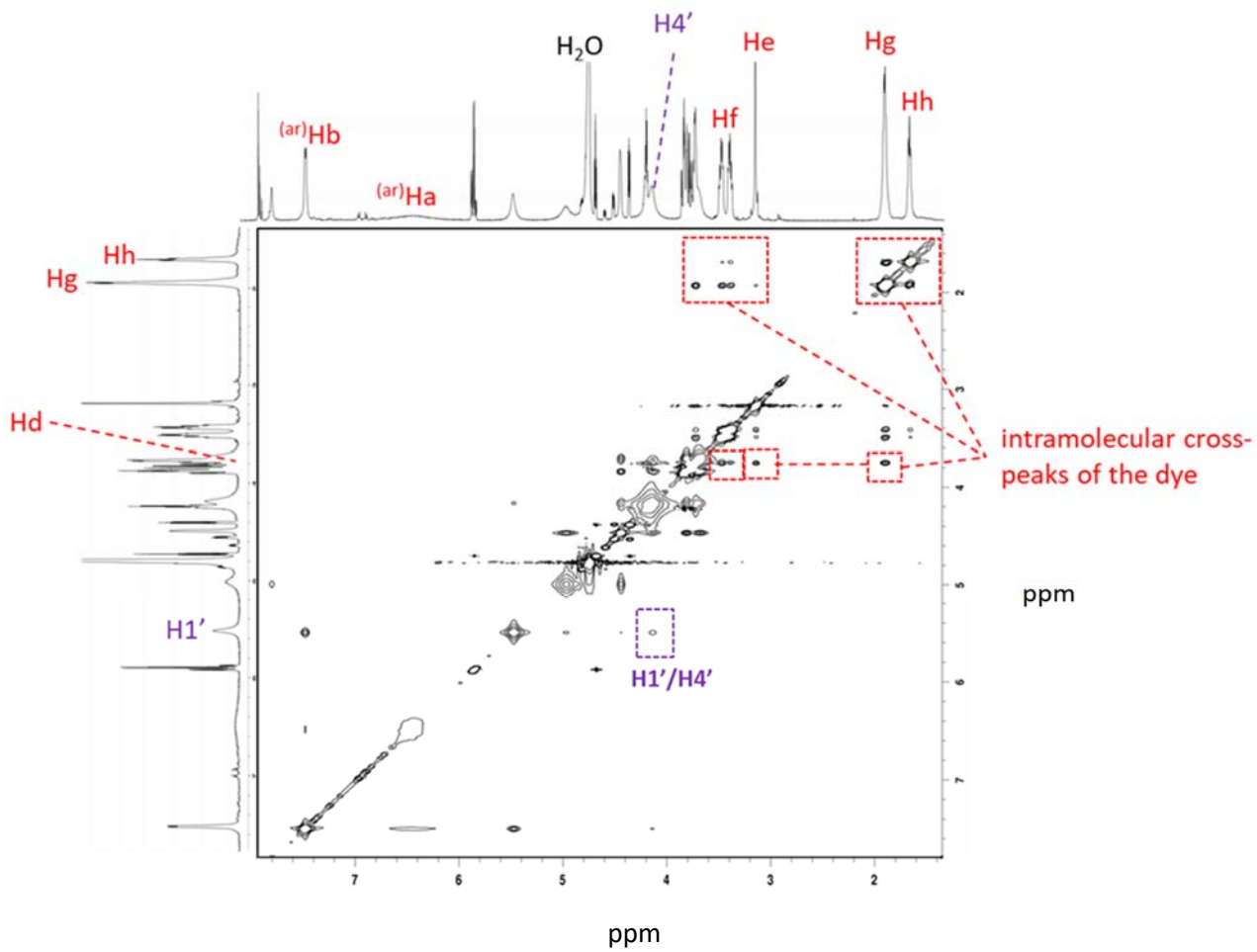


Figure S2. 2D NOESY spectrum recorded in D₂O at 25°C on the 10 mM GBK solution in the presence of **E-1** ([total-G]/[**E-1**] = 3). **(a)**: proton signals and cross-peaks corresponding to associated guanosines and **E-1** are indicated in purple and red, respectively

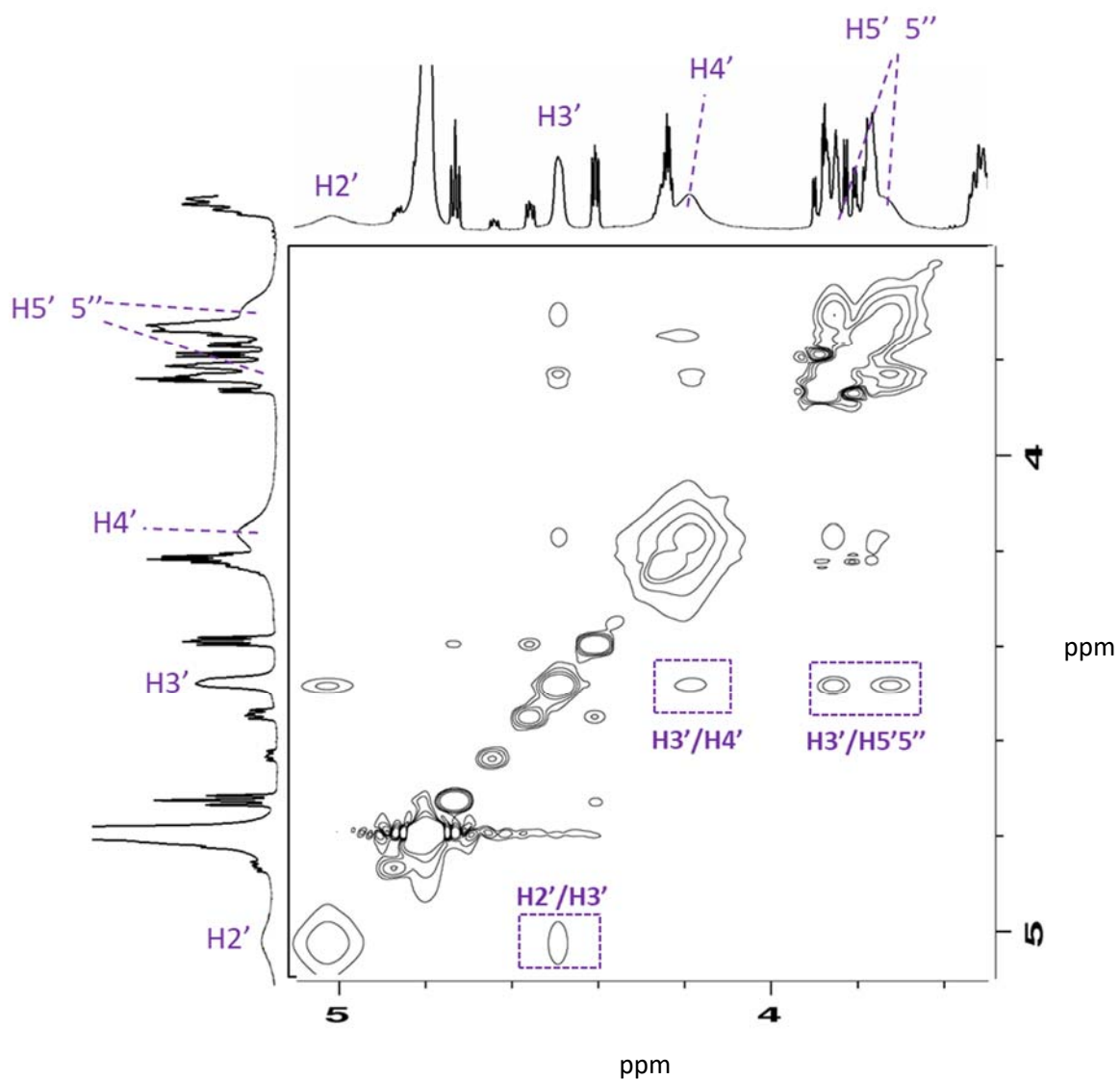


Figure S3. Enlarged view of the spectrum of figure S2. Proton signals and intramolecular cross-peaks of associated guanosines are framed in purple.

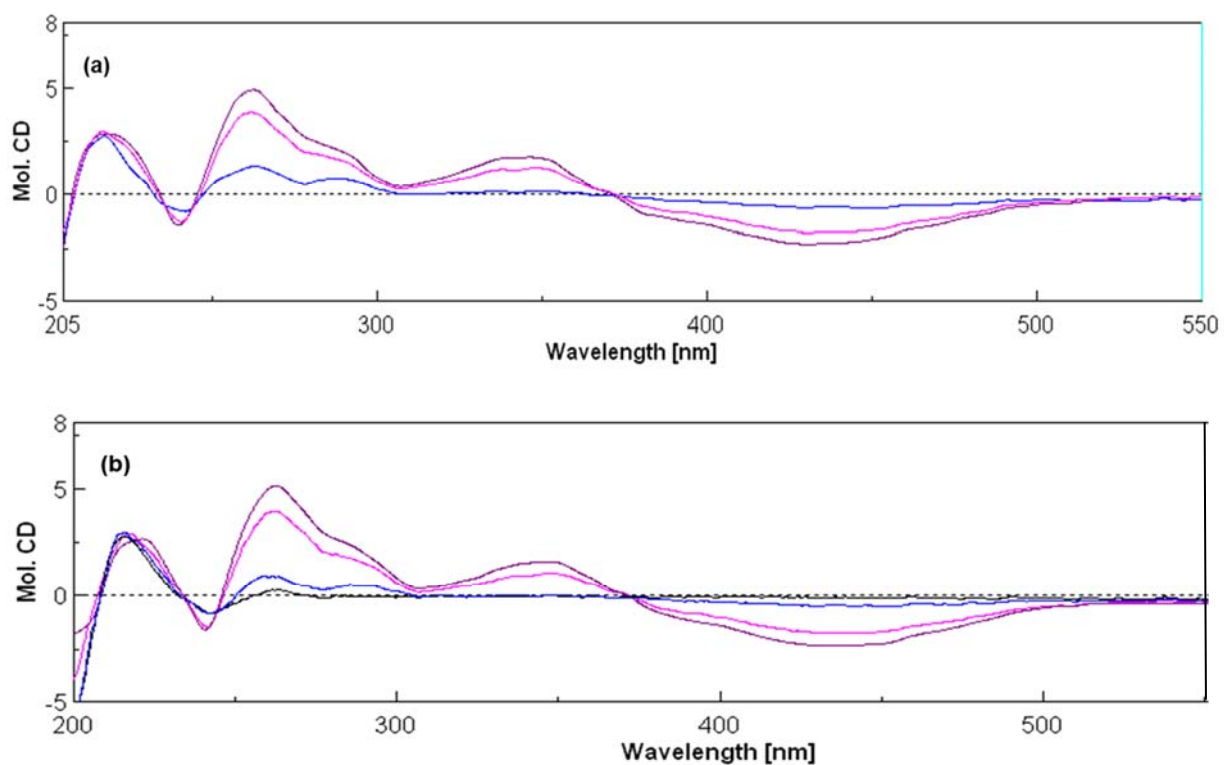


Figure S4. a) CD spectra recorded in H₂O at room temperature on the 10 mM GBK solution added with **E-1** ([total-G]/[**E-1**] = 3) before (purple line) and after irradiation at 365 nm (PSS-*cis*, blue line). The PSS-*trans* (pink line) is reached by irradiating the PSS-*cis* sample at 436 nm; b) CD spectra recorded in H₂O at room temperature on the 10 mM GBLi solution before (black line) and after addition of **E-1** ([total-G]/[**E-1**] = 3, purple line). PSS-*cis* (blue line) is reached by irradiating the GBLi/**E-1** sample at 365 nm. PSS-*trans* (pink line) is reached by irradiating the PSS-*cis* sample at 436 nm.

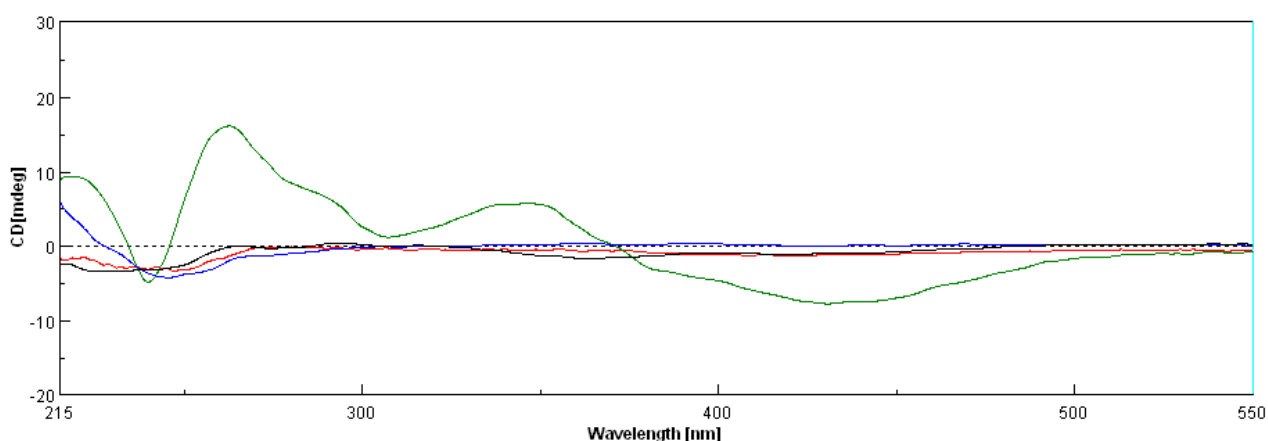


Figure S5. CD spectra recorded in H₂O at room temperature. *Green trace*: 10 mM GBK solution added with **E-1** ([total-G]/[**E-1**] = 3,); *red trace*: an analogous sample prepared as GBK, but starting from inosine instead of guanosine; *blue trace*: an analogous sample prepared as GBK, but starting from 2'-deoxyguanosine instead of guanosine; *black trace*: pure **GB** solution (10 Mm) added with **E-1** ([total-G]/[**E-1**] = 3).

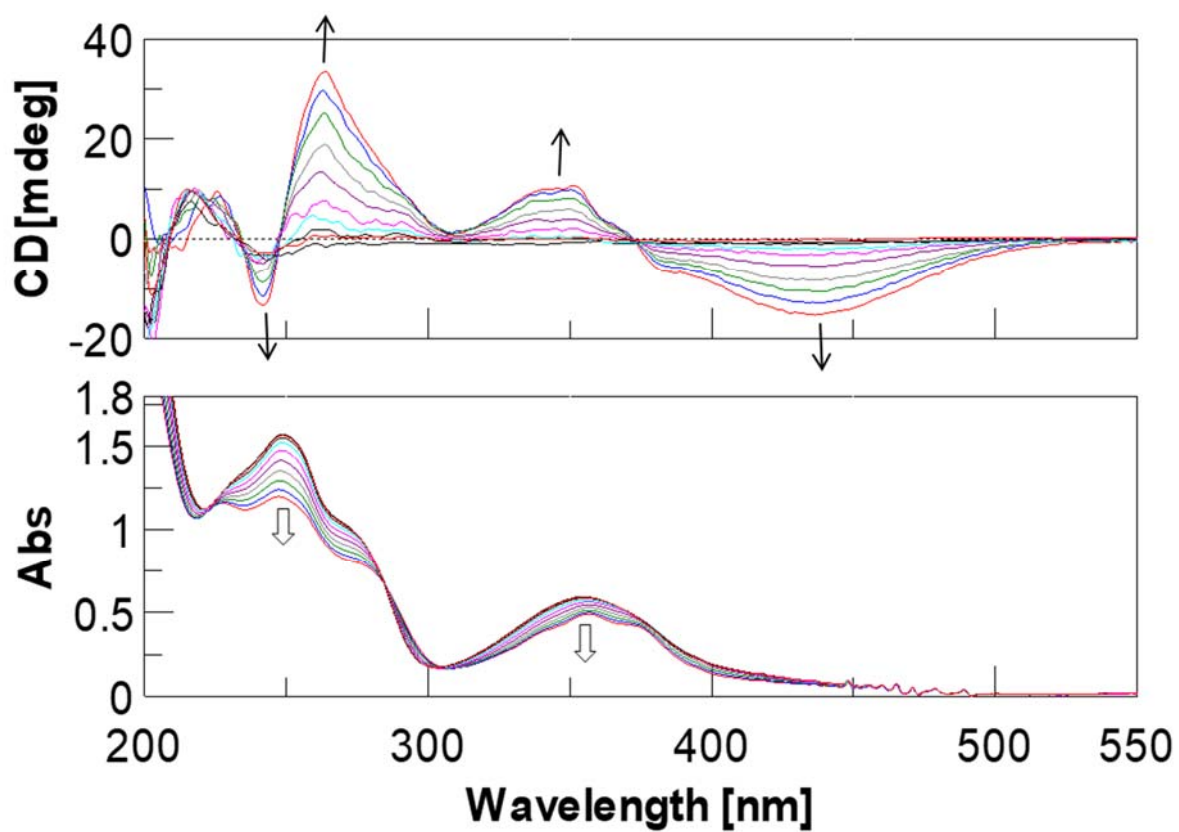


Figure S6. CD/UV spectra recorded in H₂O between 5°C and 50°C (with steps of 5°C) on the 10 mM GBK solution in the presence of **E-1** ([total-G]/[**E-1**] = 3). Arrows indicate variation of CD and UV signal intensities upon cooling.

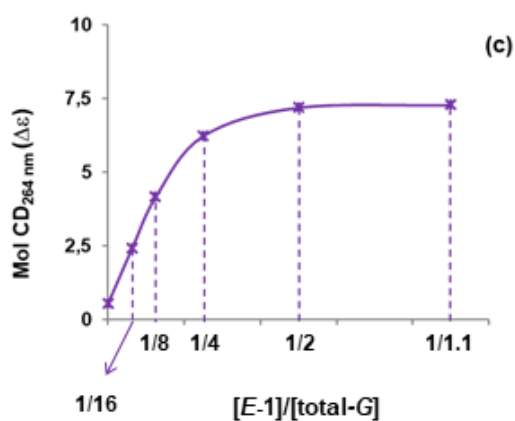
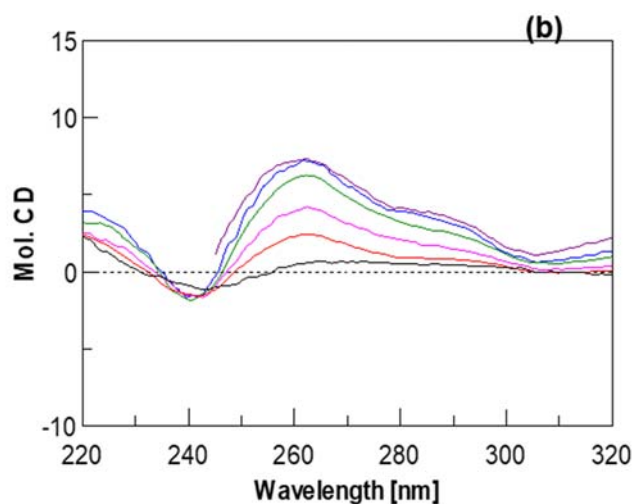
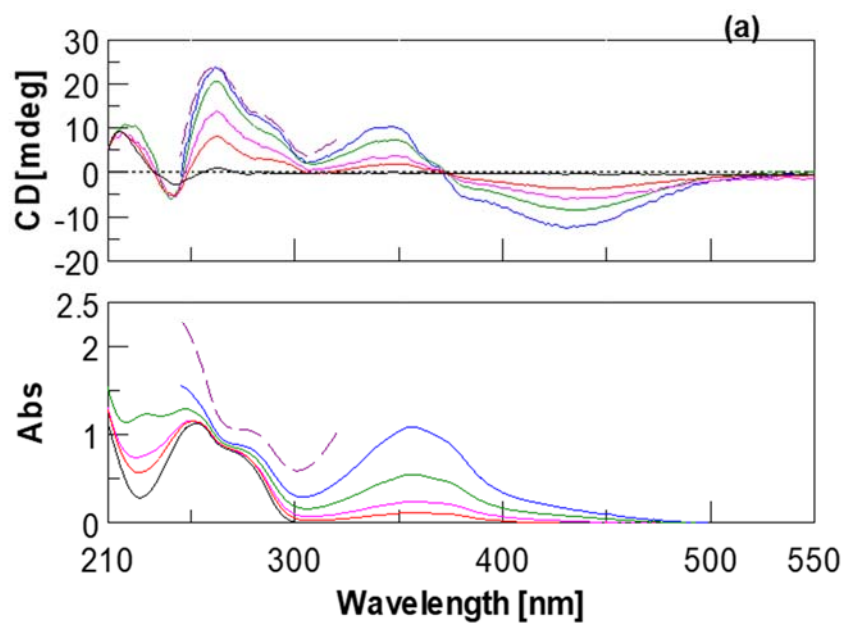


Figure S7. **(a)** and **(b)** CD (and UV) spectra recorded in H₂O at 25°C on the 10 mM GBK solution before (black line) and after addition of *E-1* 0.625 mM (red line), 1.25 mM (pink line), 2.5 mM (green line), 5 mM (blue line) and about 9 mM (purple line). Corresponding [total-G] / [*E-1*] molar ratios are 16, 8, 4, 2 and 1.1, respectively. **(c)** molecular CD detected at 264 nm plotted against concentration of added *E-1*.

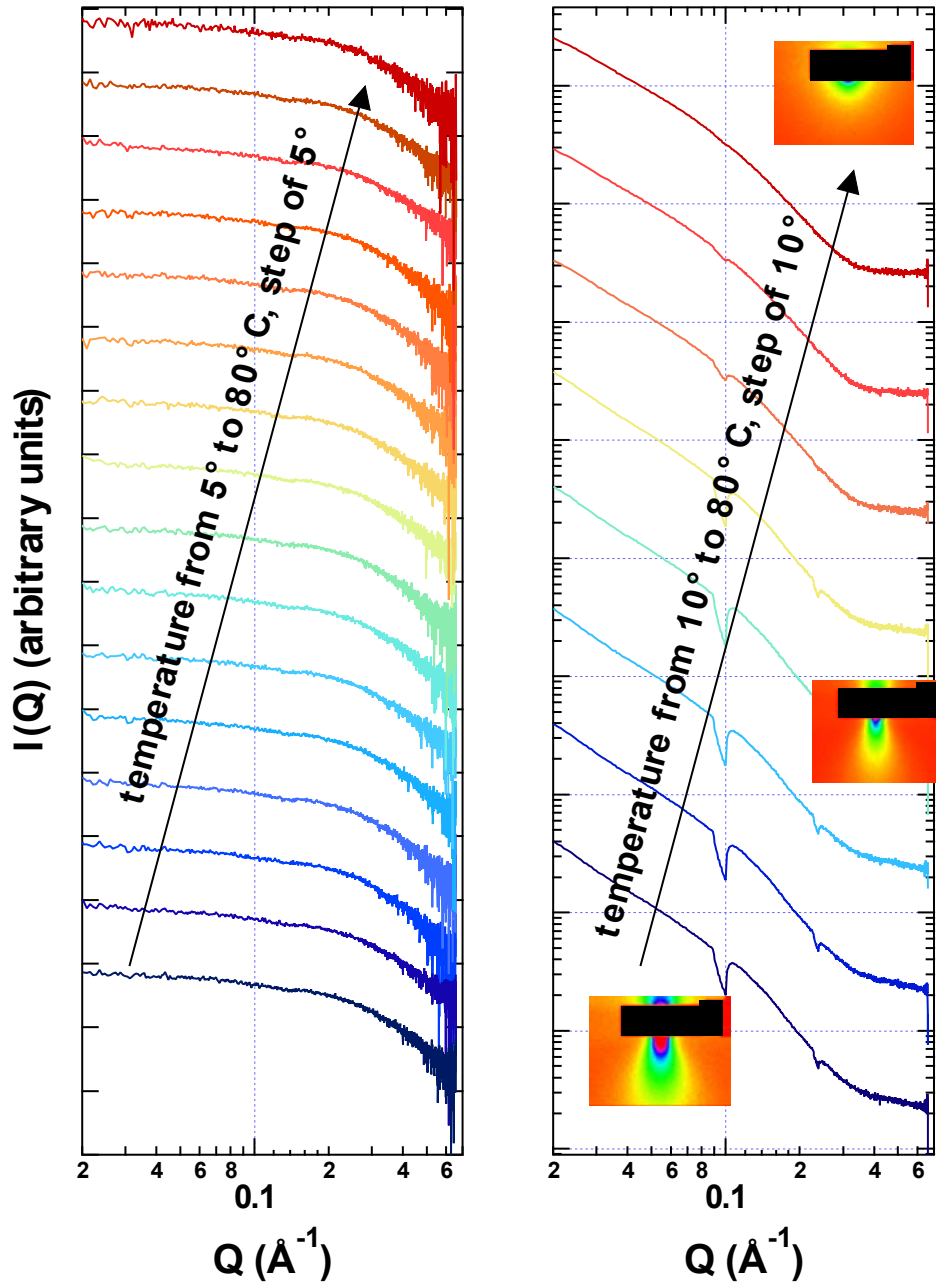


Figure S8. Variable temperature SAXS results from GBK/*E-1* samples at different composition. *Left side*: 10 mM GBK solution in the presence of *E-1* (GBK to *E-1* molar ratio is 4). Measurements have been performed from 5 to 80°C, with 5°C steps. No changes are observed: model fitting indicates that R_{core} and R are constant (6.0 ± 0.8 and 9 ± 1 Å), while the length L slightly reduces from 62 ± 3 to 53 ± 5 Å on heating. *Right side*: 20 mM GBK solution in the absence of *E-1*. Measurements have been performed from 10 to 80°C, with 10°C steps. The down spikes are artifacts due to the combination of the radial average of the intensity scattered by the oriented sample and the detector structure. The inserts show the 2D SAXS spectra observed at 10, 40 and 80°C. In these spectra, black regions are due to the beam-stop shadow.

	GBG-1	GBG-2	GB	G
GBG-1	23.3-24.4	28.2-29.1	24.8-25.1	24.1-24.7
GBG-2		34.8-35.2	29.0-29.5	28.2-29.3
GB			24.0-25.1	23.8-24.1
G				24.1-25.1

Table S1. Estimated average diameters (Å) of G-quartets formed by all possible combinations of GBK components