Supporting Information

## 1. Optical properties

Figure S1: Photos showing the colors of p-AQM molecules in chloroform solutions (a) and under UV light of 254 nm (b).

1a) Comparison of UV spectra in different solvents
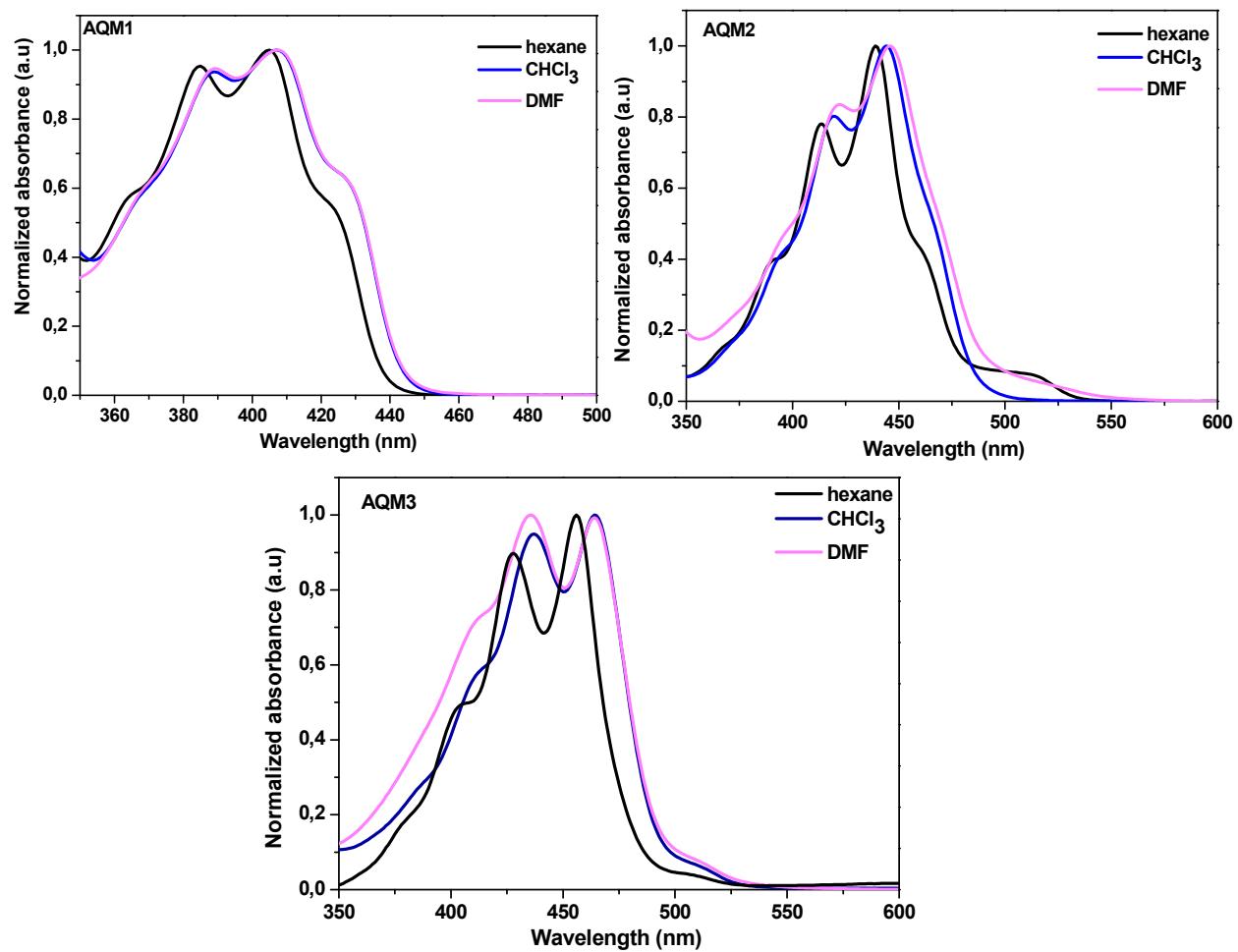
Figure S2: Normalized UV/visible absorption spectra of **AQM1**, **AQM2** and **AQM3** in different solvents

**Table S1**: Maximum absorption wavelengths of **AQM 1-3** in different solvents

	λ_{max}[nm] (AQM 1)	λ_{max} [nm] (AQM 2)	λ_{max} [nm] (AQM 3)
Hexane	405	440	456
CHCl₃	407	444	465
DMF	407	446	465

1b) Absorption spectra of non-quinoidal vs quinoidal molecules
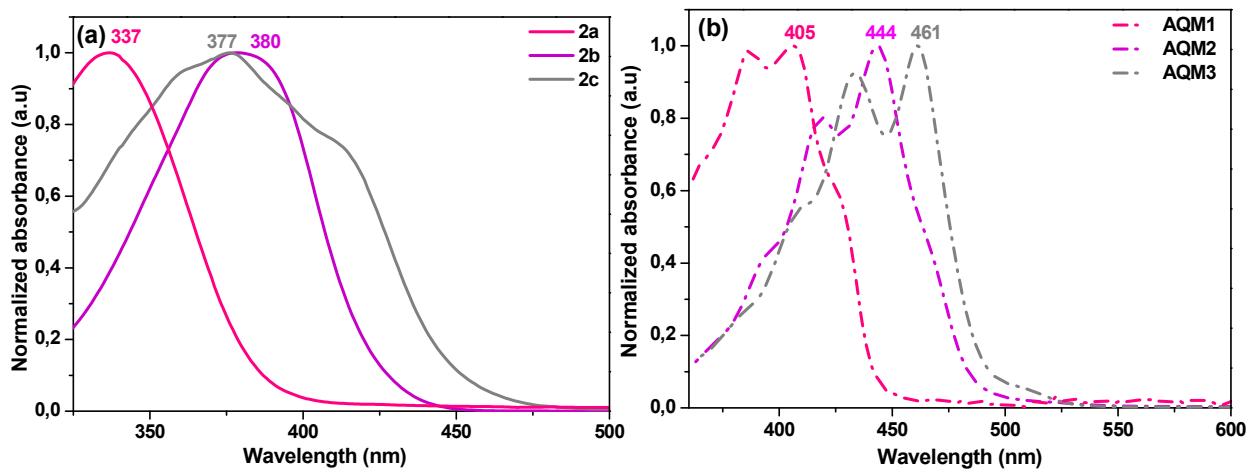
Figure S3: Comparison of normalized UV/visible absorption spectra of (a) non-quinoidal intermediates **2a-c,** and (b) p-AQM molecules in 10^{-5} M THF solution .

1c) Calculation of molar extinction coefficients
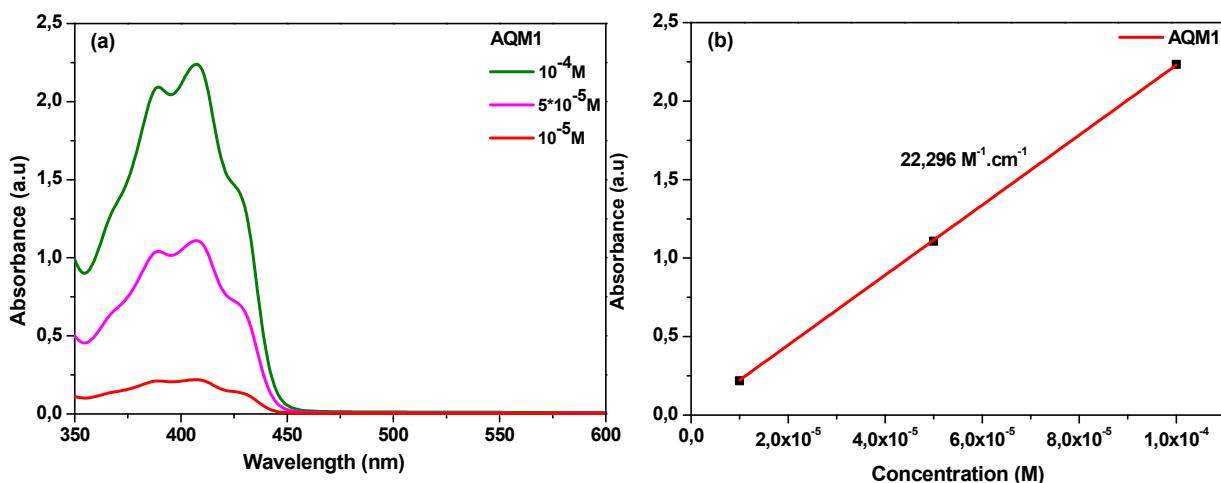
Figure S4: (a) UV/visible absorption spectra of **AQM1** at different concentrations in CHCl₃
(b) Absorbance vs Concentration plot of **AQM1** in CHCl₃
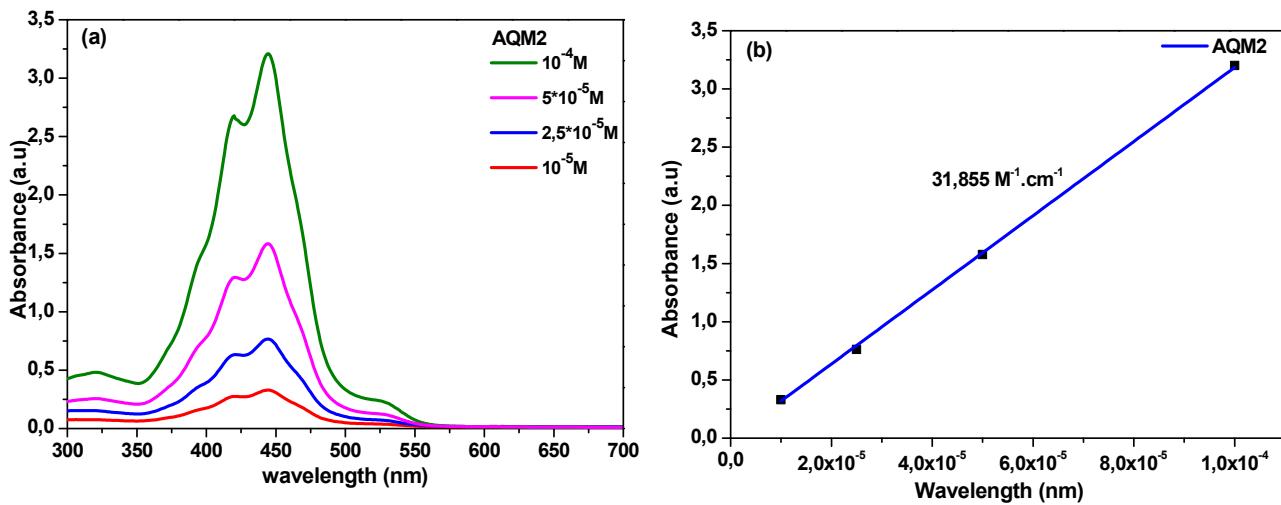
Figure S5: (a) UV/visible absorption spectra of **AQM2** at different concentrations in CHCl₃
(b) Absorbance vs Concentration plot of **AQM2** in CHCl₃
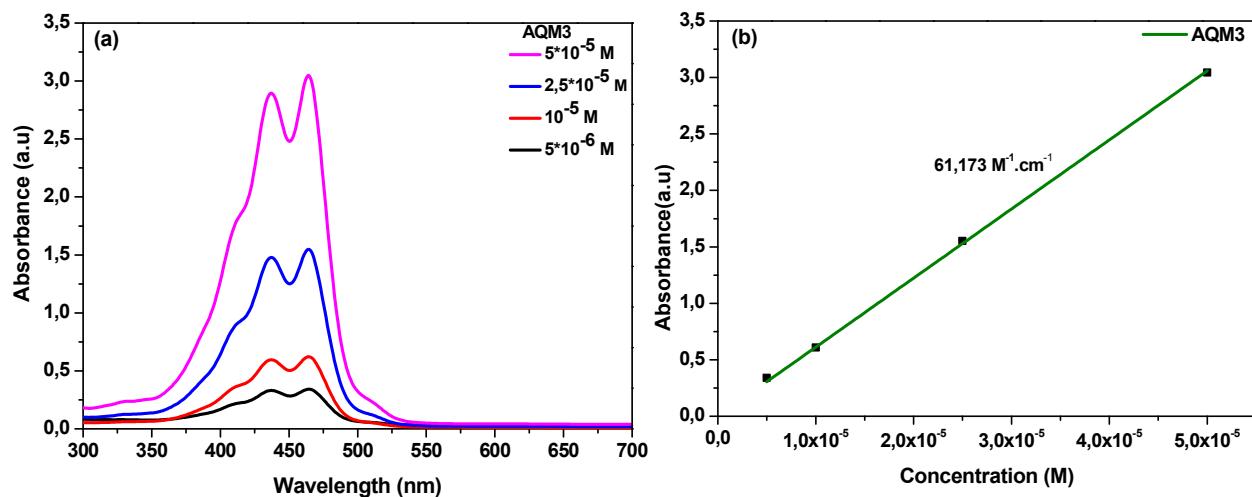
Figure S6: (a) UV/visible absorption spectra of **AQM3** at different concentrations in CHCl₃
(b) Absorbance vs Concentration plot of **AQM3** in CHCl₃

2. Thermal properties
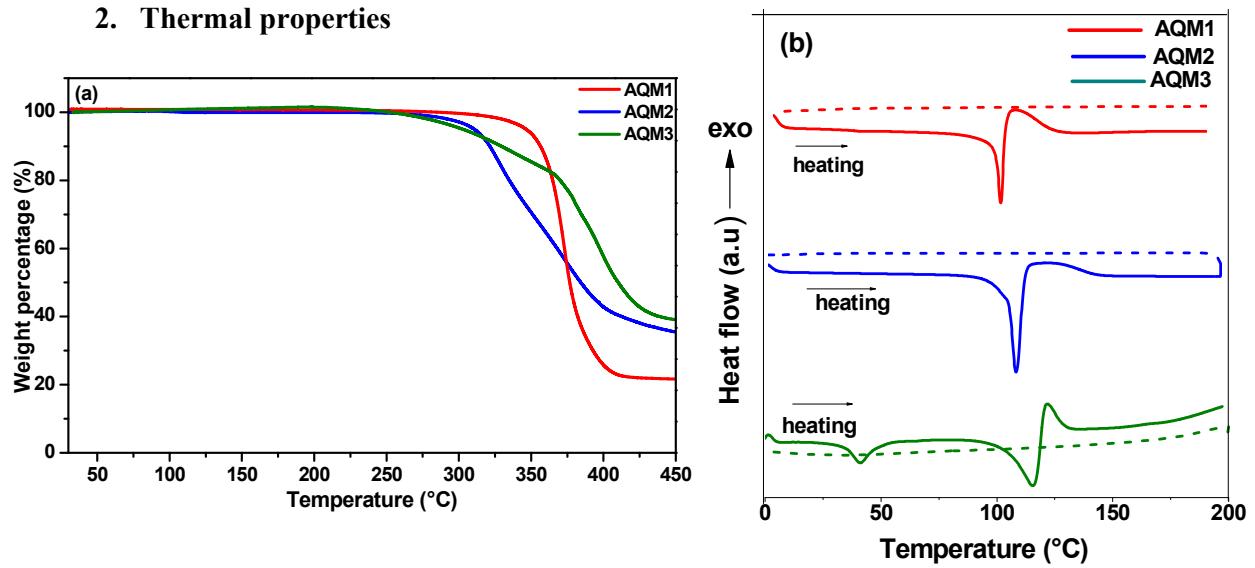
Figure S7: (a): TGA curves under nitrogen at 10 °C /min scan rate. (b): DSC curves under nitrogen: 1st heating (full line) and cooling cycles (dashed line) at 10 °C/min scan rate

Table S2: Thermal properties of p-AQM molecules

	Td (°C)	Tm^a (°C)	Tm^b (°C)
AQM1	340	105	109
AQM2	312	110	103
AQM3	292	40, 115	117

^{a}: Measured by DSC
^{b}: Measured by capillary method

3. Theoretical calculations

AQM1 and **AQM2** can exist as Z and E isomers depending on the configuration of the double bond connecting the azaquinodimethane unit with the substituents (see for example **Figure S8**). Only the symmetric isomers with the same E or Z conformations on the left and right sides of the molecule are considered for simplicity.
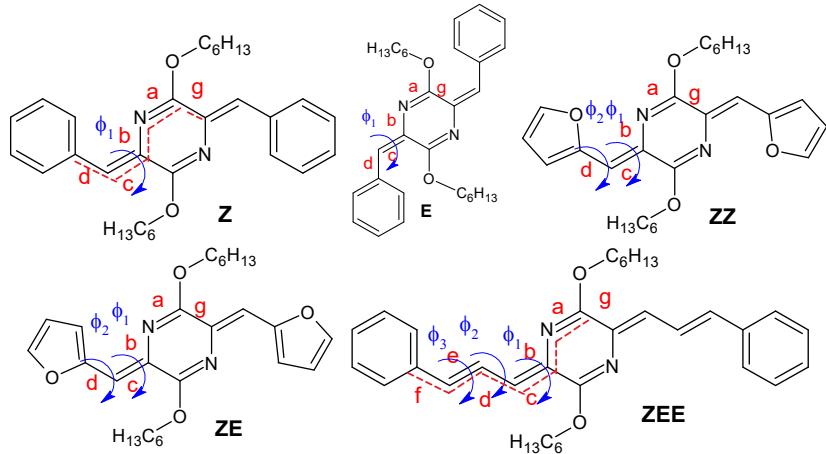

Figure S8: E, Z, ZZ, ZE and ZEE isomers displayed for **AQM1-3**

For **AQM3** due to the presence of several double bond between the phenyl groups and the central unit we calculated 8 isomers and concluded that the isomer labeled as ZEE is the most stable. Furthermore and considering the energies difference with the other isomer, i. e. more than 10 kJ/mol, the ZEE isomer is the only one that we consider to calculate the absorption spectra of this molecule. All the PBE0, B3LYP and ωB97X-D XCF give the same energetic ordering of the different isomer: Z < E for **AQM1**, ZE < ZZ < EE < EZ for **AQM2** and ZEE < EEE < ZEZ < ZZE < EEZ < ZZZ < EZE < EZZ for **AQM3** (See **Table S3**)

Table S3: Relatives energies (in kJ.mol^{-1}) of the isomers of AQM1, AQM2 and AQM3 compounds calculated at the PBE0/6-311G(d,p) and B3LYP/6-311G(d,p) levels.

AQM1	Z	E						
PBE0	0	54.9						
B3LYP	0	54.1						
ωB97XD	0	40.8						
AQM2	**ZE**	**EE**	**ZZ**	**EZ**				
PBE0	0	50.1	14.9	60.3				
B3LYP	0	49.3	13.6	58.9				
ωB97XD	0	50.0	21.1	57.8				
AQM3	**EEE**	**EEZ**	**ZEE**	**ZEZ**	**EZE**	**ZZE**	**ZZZ**	**EZZ**
PBE0	23.8	56.9	0	29.8	86.5	30.1	79.3	117.9
B3LYP	24.0	58.3	0	31.9	88.1	33.6	91.7	128.5
ωB97XD	21.3	47.0	0	19.1	50.9	18.2	27.3	48.9

AQM1 (Z)   AQM1 (E)   AQM2 (ZE) AQM2 (EE)   AQM3 (ZEE)
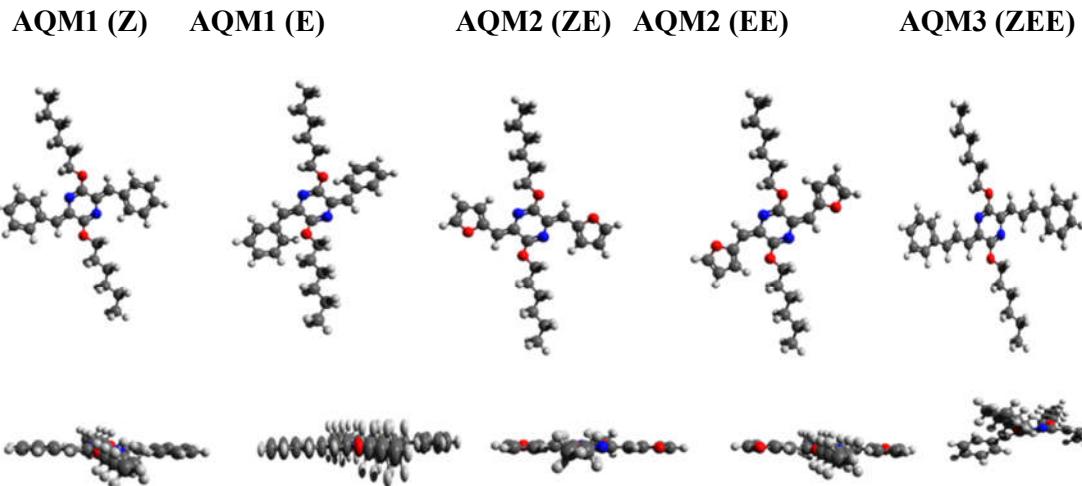
Figure S9. Optimized geometries of the isomers of AQM1, AQM2 and AQM3 (ZEE) compounds (PBE0/6-311G(d,p) calculations) (top view and side view).

Table S4: Geometric parameters of the isomers of AQM1, AQM2 and AQM3 compounds calculated at the PBE0/6-311G(d,p) and B3LYP/6-311G(d,p) levels.

	a	B	c	D	e	f	g	$\phi1$	$\phi2$	$\phi3$	BLA
AQM1											
PBE0											
Z	1.285	1.382	1.361	1.450			1.466	0.0			0.110
E	1.282	1.391	1.357	1.458			1.469	173.4			0.120
B3LYP											
Z	1.288	1.389	1.368	1.455			1.473	0.0			0.111
E	1.285	1.398	1.361	1.462			1.476	173.2			0.122
ωB97XD											
Z	1.280	1.391	1.351	1.461			1.476	0.0			1.127
E	1.278	1.401	1.345	1.472			1.482	174.3			0.140
AQM2											
PBE0											
ZE	1.287	1.381	1.363	1.423			1.460	0	180.0		0.096
EE	1.284	1.386	1.367	1.458			1.458	180.0	180.0		0.108
ZZ	1.285	1.379	1.363	1.423			1.463	0.4	0.3		0.098
EZ	1.284	1.387	1.363	1.426			1.465	172.1	11.6		0.102
B3LYP											
ZE	1.290	1.387	1.367	1.426			1.466	0.0	180.0		0.098
EE	1.287	1.393	1.372	1.428			1.463	178.9	179.0		0.098
ZZ	1.288	1.385	1.367	1.426			1.468	0.0	0.0		0.099
EZ	1.288	1.394	1.367	1.429			1.470	171.8	11.4		0.103
ωB97XD											
ZE	1.281	1.389	1.352	1.435			1.470	0.0	180.0		0.115
EE	1.278	1.397	1.355	1.439			1.469	177.6	174.8		0.118
ZZ	1.279	1.388	1.352	1.435			1.473	0.0	0.0		0.116
EZ	1.279	1.398	1.348	1.444			1.479	172.1	26.3		0.127

| AQM3										
PBE0										
EEE	1.285	1.383	1.370	1.425	1.355	1.453	1.461	180.0	180.0	180.0	0.094
EEZ	1.284	1.384	1.369	1.430	1.357	1.460	1.463	175.9	174.0	7.0	0.097
ZEE	1.286	1.380	1.366	1.426	1.353	1.454	1.461	0.0	180.0	180.0	0.095
ZEZ	1.286	1.388	1.366	1.430	1.355	1.461	1.463	2.8	175.7	6.2	0.100
EZE	1.284	1.386	1.368	1.437	1.350	1.456	1.464	173.5	26.0	177.0	0.102
ZZE	1.288	1.378	1.369	1.434	1.355	1.455	1.461	0.1	0.9	179.9	0.095
ZZZ	1.285	1.378	1.362	1.444	1.352	1.459	1.467	1.4	40.7	8.8	0.104
EZZ	1.283	1.388	1.359	1.449	1.347	1.463	1.468	176.6	46.2	2.4	0.112
B3LYP										
EEE	1.288	1.390	1.374	1.428	1.359	1.457	1.466	180.0	180.0	180.0	0.095
EEZ	1.288	1.391	1.373	1.433	1.360	1.465	1.468	175.9	175.3	6.8	0.099
ZEE	1.290	1.387	1.371	1.429	1.356	1.458	1.466	0.0	180.0	180.0	0.096
ZEZ	1.289	1.387	1.370	1.433	1.358	1.465	1.468	2.8	176.3	6.0	0.099
EZE	1.287	1.393	1.373	1.441	1.354	1.460	1.469	172.8	23.6	176.4	0.103
ZZE	1.292	1.385	1.373	1.437	1.358	1.460	1.467	0.2	1.0	179.9	0.096
ZZZ	1.288	1.385	1.364	1.449	1.354	1.464	1.473	1.0	42.7	8.6	0.107
EZZ	1.286	1.396	1.362	1.454	1.350	1.467	1.473	178.1	49.2	2.7	0.115
ωB97XD										
EEE	1.279	1.396	1.357	1.441	1.345	1.465	1.473	180.0	180.0	180.0	0.117
EEZ	1.278	1.396	1.355	1.446	1.346	1.472	1.473	176.7	170.8	5.7	0.120
ZEE	1.280	1.392	1.353	1.440	1.344	1.466	1.472	0.0	180.0	180.0	0.117
ZEZ	1.280	1.392	1.352	1.445	1.345	1.473	1.473	2.0	173.4	4.9	0.120
EZE	1.278	1.401	1.349	1.457	1.340	1.468	1.483	171.9	38.2	176.5	0.130
ZZE	1.282	1.387	1.356	1.449	1.347	1.466	1.470	0.0	0.4	180.0	0.115
ZZZ	1.280	1.386	1.350	1.456	1.344	1.469	1.476	1.8	42.2	5.6	0.122
EZZ	1.278	1.400	1.346	1.463	1.341	1.473	1.478	175.2	44.8	0.8	0.132

Energies of the HOMO and LUMO orbitals

Table S5: Energies (in eV) of HOMO, LUMO and HOMO/LUMO gap of the isomers of AQM1, AQM2 and AQM3 compounds calculated at the PBE0/6-311G(d,p), B3LYP/6-311G(d,p) and ωB97XD/6-311G(d,p) levels.

	HOMO	LUMO	HOMO/LUMO gap
AQM1			
PBE0			
Z	-5.646	-2.382	3.263
E	-5.738	-2.261	3.477
B3LYP			
Z	-5.435	-2.474	2.961
E	-5.516	-2.474	3.04
ωB97XD			
Z	-7.230	-0.827	6.403
E	-7.541	-0.443	7.098
AQM2			
PBE0			
ZE	-5.319	-2.344	2.975

EE	-5.239	-2.344	2.895
ZZ	-5.277	-2.283	2.994
EZ	-5.278	-2.260	3.018
B3LYP			
ZE	-5.141	-2.460	2.681
EE	-5.066	-2.462	2.603
ZZ	-5.099	-2.400	2.698
EZ	-5.099	-2.384	2.715
ωB97XD			
ZE	-6.940	-0.823	6.116
EE	-6.855	-0.819	6.036
ZZ	-6.879	-0.763	6.116
EZ	-7.085	-0.608	6.477
AQM3			
PBE0			
EEE	-5.241	-2.632	2.609
EEZ	-5.370	-2.575	2.795
ZEE	-5.305	-2.574	2.734
ZEZ	-5.592	-2.540	3.051
EZE	-5.358	-2.609	2.748
ZZE	-5.321	-2.679	2.642
ZZZ	-5.592	-2.437	3.155
EZZ	-5.585	-2.381	3.203
B3LYP			
EEE	-5.053	-2.714	2.340
EEZ	-5.177	-2.680	2.497
ZEE	-5.114	-2.658	2.456
ZEZ	-5.239	-2.647	2.592
EZE	-5.150	-2.713	2.437
ZZE	-5.128	-2.760	2.367
ZZZ	-5.391	-2.519	7.910
EZZ	-5.390	-2.494	2.896
ωB97XD			
EEE	-6.783	-1.095	5.691
EEZ	-6.969	-0.959	6.010
ZEE	-6.871	-1.020	5.851
ZEZ	-7.046	-0.906	6.140
EZE	-7.273	-0.705	6.568
ZZE	-6.903	-1.133	5.770
ZZZ	-7.265	-0.781	6.484
EZZ	-7.376	-0.617	6.759

AQM1

Z

HOMO   LUMO

E

HOMO   LUMO

AQM2

ZE

HOMO   LUMO

EE

HOMO   LUMO

AQM3 (ZEE isomer)

HOMO   LUMO
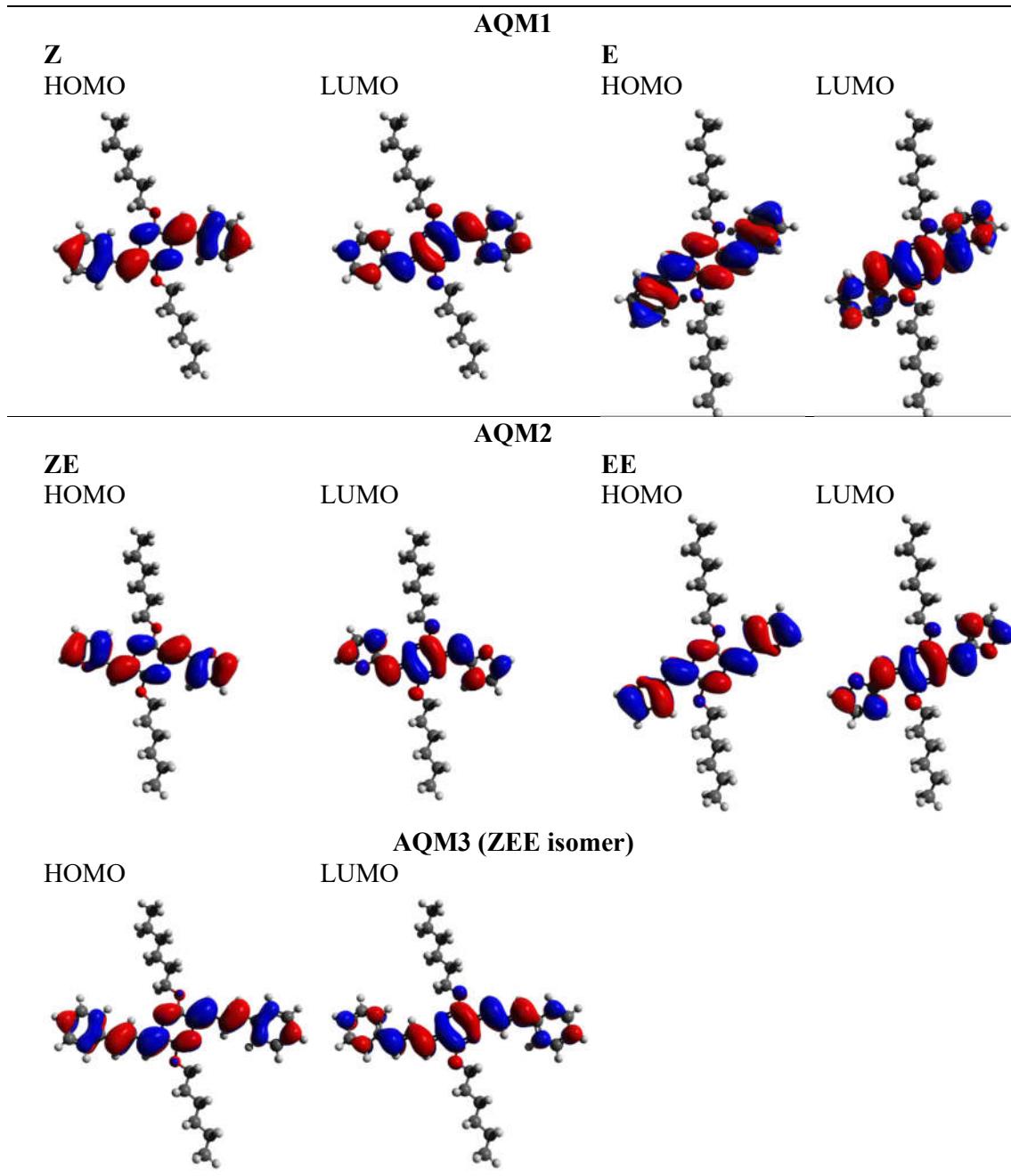
Figure S10. HOMO and LUMO orbitals for AQM1, AQM2 and AQM3 obtained at the PBE0/6-311G(d,p) level of calculations

To get a first qualitative idea of the TDDFT performance with respect to this family of compounds, we startby computing their TDDFT vertical absorption spectra in chloroform solvent from their ground-state optimized structures (**Figure S11**) either with PBE0, B3LYP or ωB97XD functionals. The results are compiled in **Table S6**. The Z, ZE and ZEE isomers of **AQM1**, **AQM2** and **AQM3** were used for this study.

It is clear that CAM-B3LYP, M062X and ωB97XD functionals provide almost similar results and the better agreement with experimental data for the lowest maximum absorption. The PBE0, B3LYP and M06 are dismissed due to the large red-shift in the absorption energies. Following this study, we selected

the ωB97XD functional to calculate the excited state energies in combination with the geometries calculated with PBE0. The calculated $S_0 \rightarrow S_1$ energies using the combination are found to be 465 nm for AQM3 (463 nm exptl), 408 nm for AQM1 (400 nm exptl) and 434 nm for AQM2 (446 nm exptl)

Table S6: Benchmark on transitions for **AQM3** (ZEE isomer), **AQM1** (Z isomer) and **AQM2 (ZE isomer)** compounds. The ground state geometries were computed using the 6-311G(d,p) basis-set using PBE0, B3LYP and ωB97XD functionals.

	AQM3		AQM1		AQM2	
	PBE0/6-311G(d,p)					
	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f
PBE0	510	2.494	427	1.681	460	1.513
B3LYP	523	2.443	437	1.645	469	1.481
CAM-B3LYP	470	2.583	402	1.751	435	1.561
M06	518	2.448	435	1.644	467	1.483
M062X	468	2.561	399	1.746	433	1.554
ωB97XD	465	2.588	400	1.751	434	1.564
Exptl	463		408		446	
	B3LYP/6-311G(d,p)					
	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f
PBE0	512	2.502	429	1.687	463	1.527
B3LYP	526	2.451	439	1.651	472	1.495
CAM-B3LYP	472	2.592	403	1.759	437	1.575
M06	521	2.455	437	1.651	470	1.496
M062X	470	2.570	400	1.754	435	1.568
ωB97XD	468	2.597	401	1.759	436	1.589
Exptl	463		408		446	
	ωB97XD /6-311G(d,p)					
	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f	$S_0 \rightarrow S_1$	f
PBE0	480	2.433	412	1.653	443	1.469
B3LYP	493	2.376	422	1.615	452	1.436
CAM-B3LYP	438	2.555	386	1.734	415	1.527
M06	487	2.394	420	1.619	449	1.442
M062X	437	2.528	383	1.728	414	1.518
ωB97XD	434	2.564	394	1.736	414	1.532
Exptl	463		408		446	

Figure S11: TD-DFT calculations of the absorption spectra of **AQM1** (Z), **AQM2** (ZE) and **AQM3** (ZEE)

Table S7: Lowest electronic transition energies calculated for AQM3, AQM1 and AQM2 compounds at the ωB97XD/6-311G(d,p) PBE1PBE/6-311G(d,p).

|	**AQM3**	
	$S_0 \rightarrow S_1$	*f*
EEE	482	2.569
EEZ	456	2.718
ZEE	465	2.588
EZE	475	2.610
ZEZ	443	2.798
ZZZ	427	2.903
EZZ	428	2.898
ZZE	492	2.521
Exptl	463	
	AQM1	
Z	400	1.7512
E	383	1.555
Exptl	408	
	AQM2	
ZE	434	1.564
EE	442	1.797
ZZ	427	1.711
EZ	431	1.534
Exptl	446	

Table S8: Lowest electronic transition energies in absorption and emission calculated for **AQM3** (ZEE isomer), **AQM1** (Z isomer) and **AQM2** (ZE isomer) compounds at the ωB97XD/6-311G(d,p) PBE1PBE/6-311G(d,p) level.

	Absorption		**Emission**	
	$S_0 \rightarrow S_1$	*f*	$S_1 \rightarrow S_0$	*f*
AQM1	400	1.751	481	2.250
AQM2	434	1.564	512	2.420
AQM3	465	2.588	626	1.981

Redox potentials

DFT calculations were also performed to determine the redox potentials in chloroform according to the thermodynamic cycle shown below:

$$M^+(gas) \xrightarrow{\Delta G^{gas}_{redox}} M(gas)$$

$$\Delta G_{CHCl3}(M^+) \downarrow \qquad\qquad \downarrow \Delta G_{CHCl3}(M)$$

$$M^+(CHCl_3) \xrightarrow{\Delta G^{CHCL3}_{redox}} M(CHCl_3)$$

$$\Delta G^{CHCL3}_{redox} = \Delta G^{gas}_{redox} + \Delta G^{CHCL3}(M^+) - \Delta G^{CHCL3}(M)$$

$$\Delta G^{CHCL3}_{redox} = \Delta G^{gas}_{redox} + \Delta\Delta G_{sol}$$
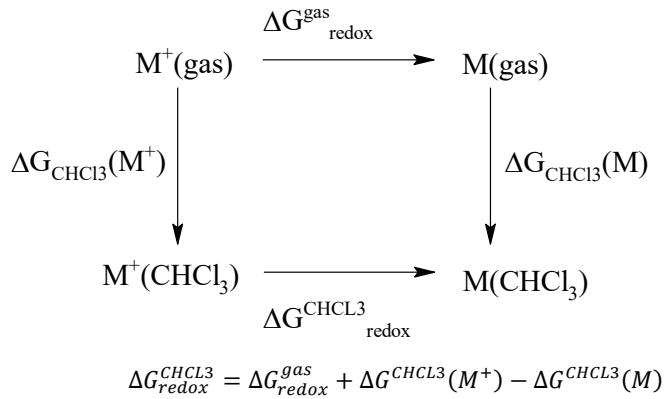
Where

$$\Delta G^{gas}_{redox} = G^{gas}(M) - G^{gas}(M^+)$$

And

$$\Delta\Delta G_{sol} = \Delta G^{CHCL3}(M^+) - \Delta G^{CHCL3}(M)$$

And the redox potential is related to $\Delta G_{redox}(CHCl3)$ as $\Delta G^{CHCL3}_{redox} = -FE^{\circ}_{redox}$
Where F is the Faraday constant, 23.06 kcal.mol^{-1} V^{-1}. The standard hydrogen electrode potential, V_{SHE} was taken as 4.43 eV [1].

From the lowest isomers of **AQM1**, **AQM2** and **AQM3**, i.e. Z, ZE and ZEE isomers respectively, the redox potentials were calculated in chloroform according to the thermodynamic cycle shown above. Results are gathered in **Table S9** and compared with the experimental ones.

Table S9. Computed redox potentials vs. experimental ones of the **AQM1**, **AQM2** and **AQM3** compounds. For each compound, calculation were performed on the most stable isomer at the PBE0/6-311(g,d) level.

	AQM1	AQM2	AQM3
Calc E (V vs SCE)	1.00	0.72	0.67
Exp E (V vs SCE)	0.72	0.64	0.72

The calculated results obtained for **AQM2** and **AQM3** are in relatively good agreement with the experimental ones measured by cyclic voltammetry with an error less than 0.08 V. Concerning **AQM1** the agreement is less satisfactory and the calculated error is 0.28 V.

4. NMR spectra
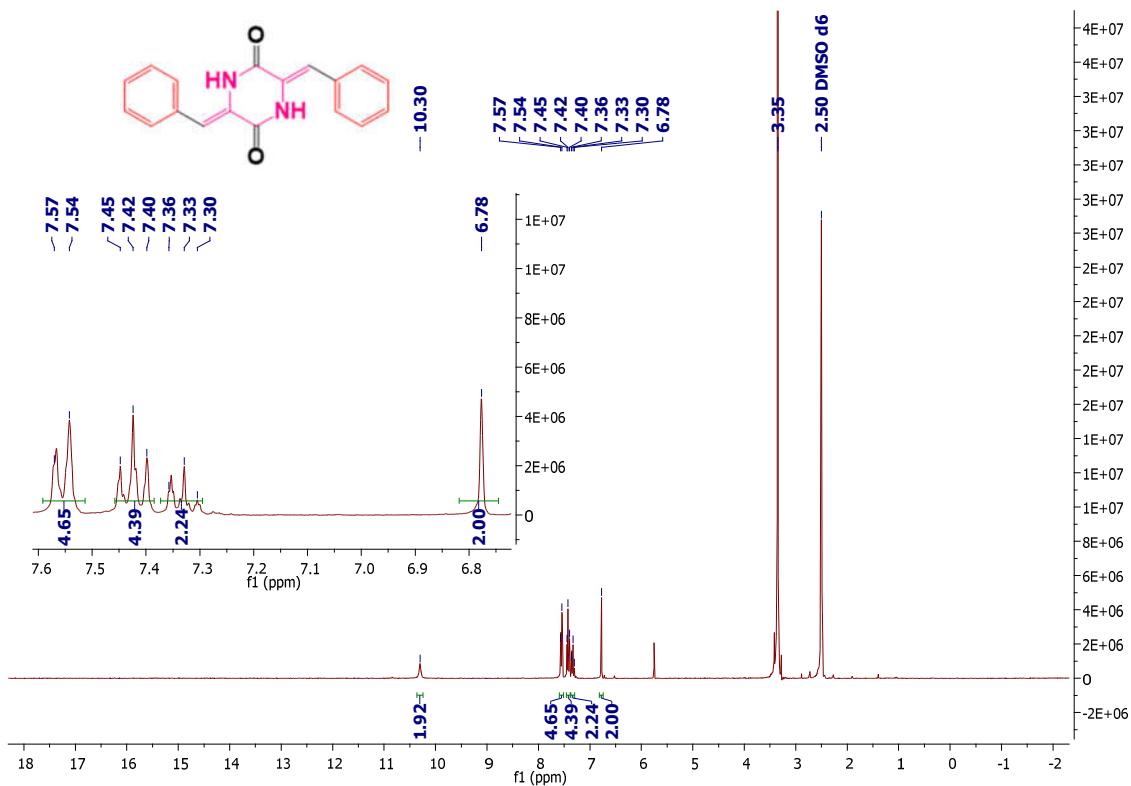
Figure S12: ^{1}H NMR spectrum of **2a** (DMSO d$_6$, 300 MHz)
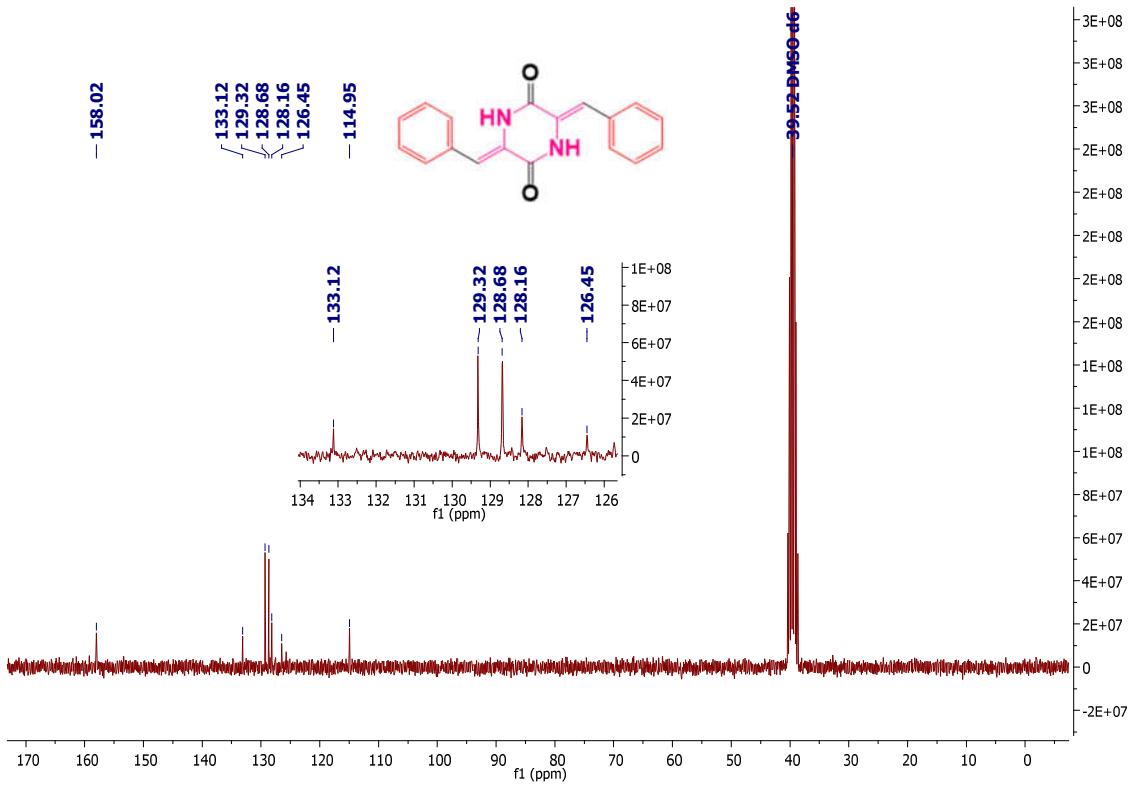
Figure S13: ^{13}C NMR spectrum of **2a** (DMSO d$_6$, 75 MHz)

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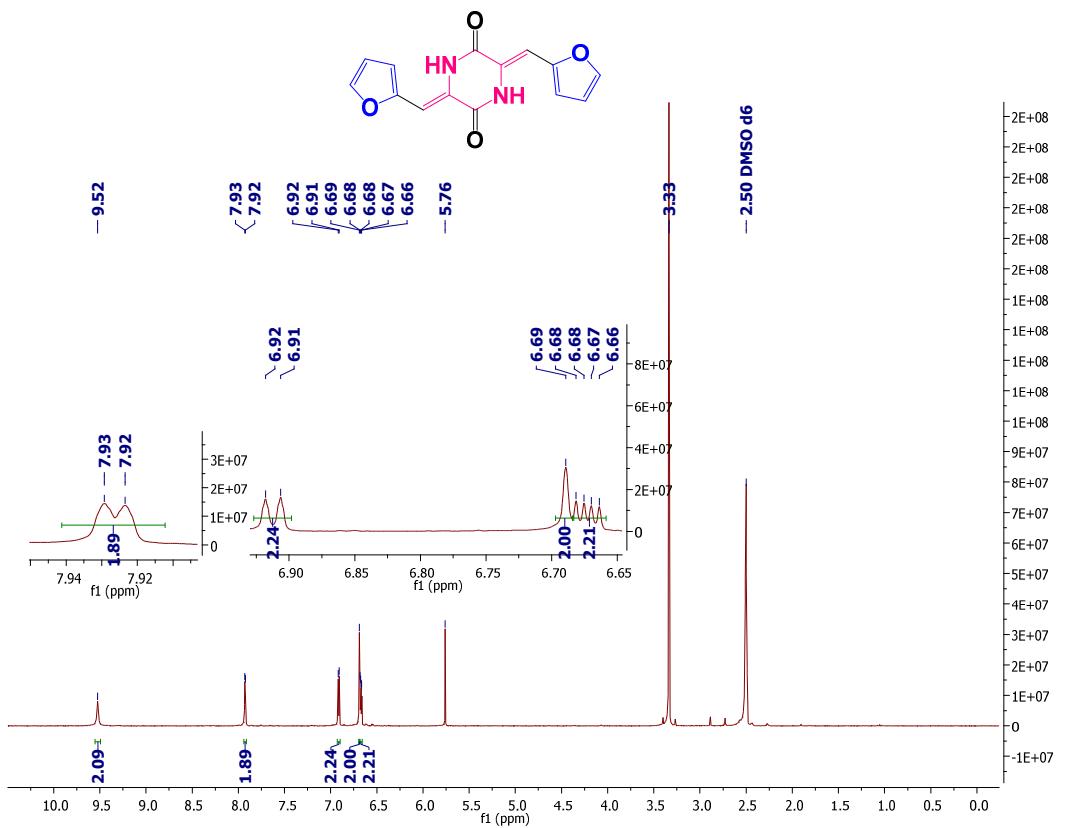
Figure S14: ^{1}H NMR spectrum of **2b** (DMSO d$_6$, 300 MHz)
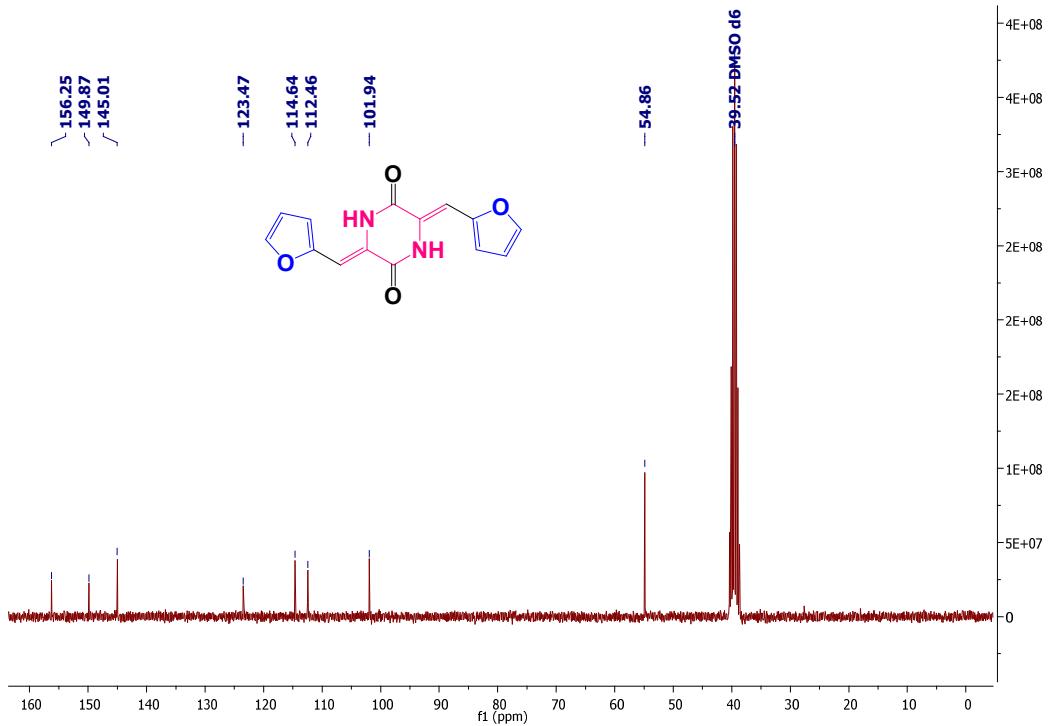
Figure S15: ^{13}C NMR spectrum of **2b** (DMSO d$_6$, 75 MHz)
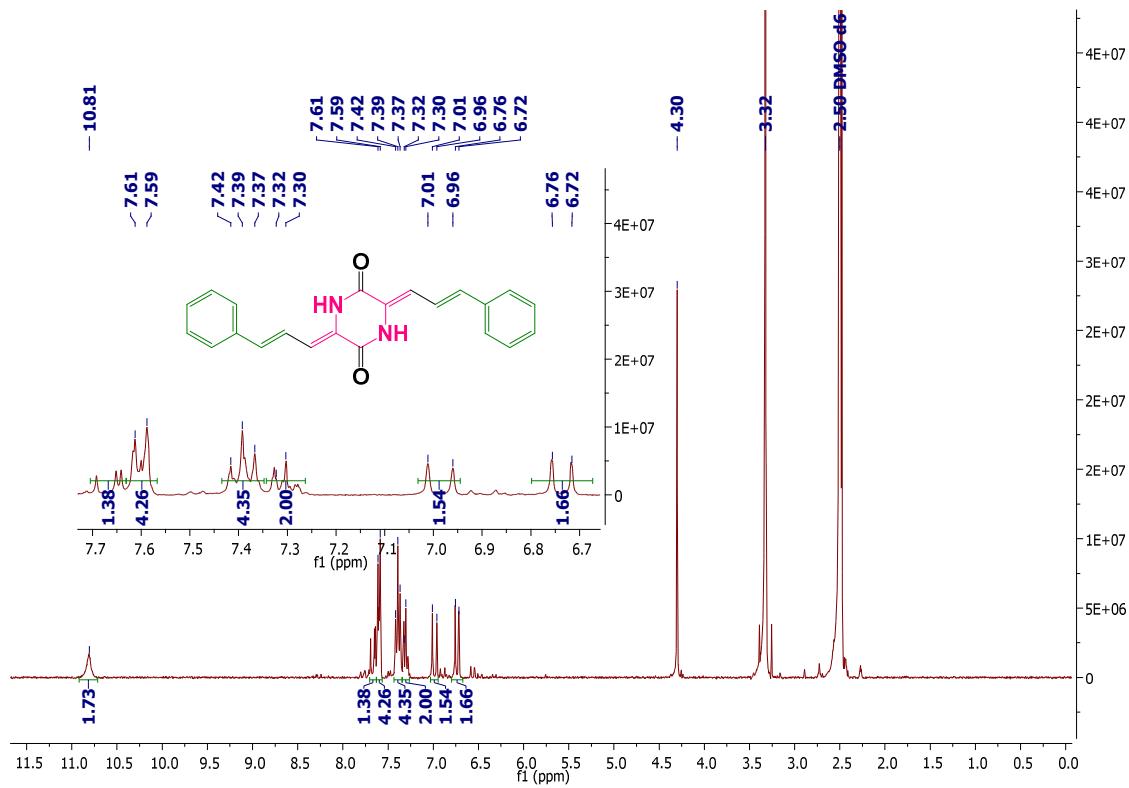
Figure S16: ^{1}H NMR spectrum of **2c** (DMSO d$_6$, 300 MHz)
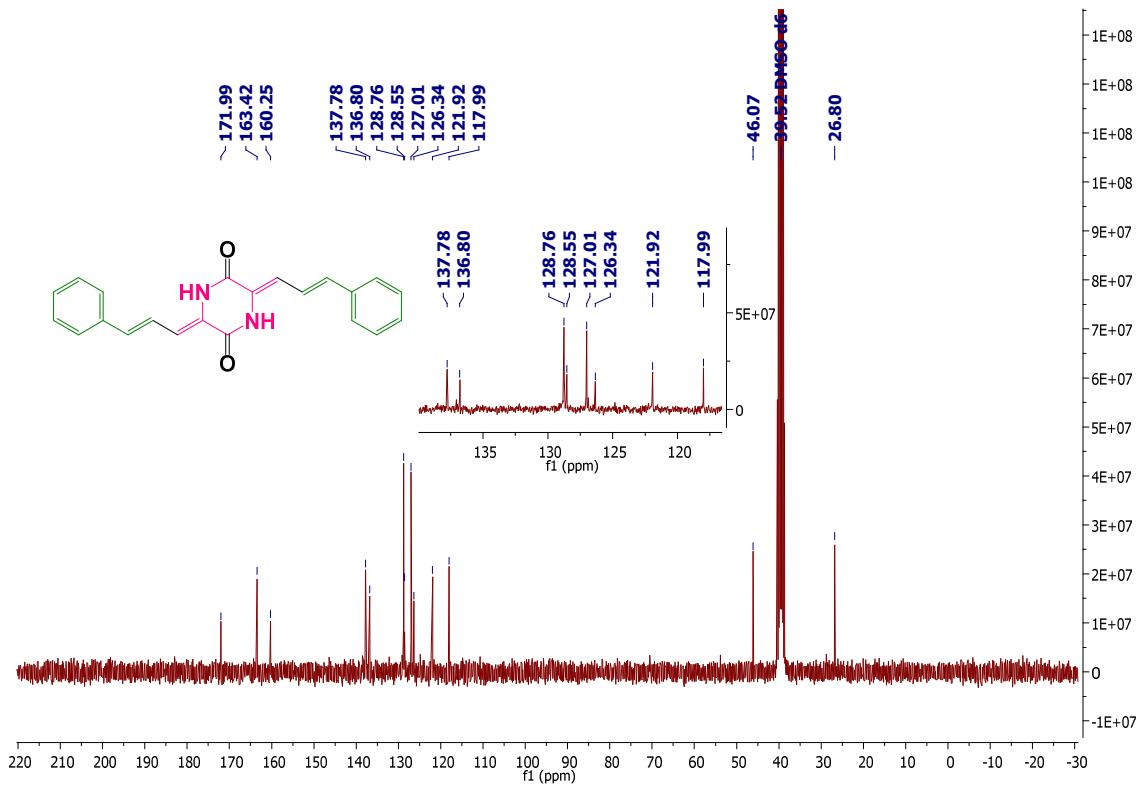
Figure S17: ^{13}C NMR spectrum of **2c** (DMSO d$_6$, 75 MHz)
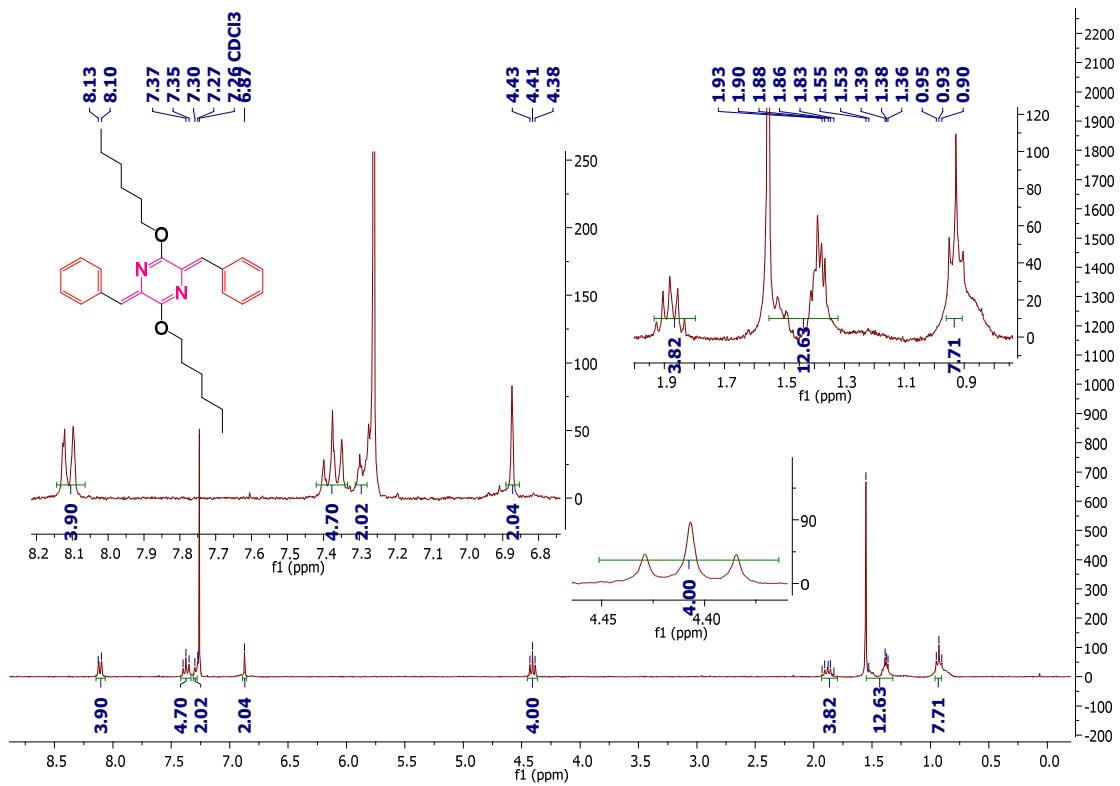
Figure S18: ^{1}H NMR spectrum of **AQM1** (CDCl$_3$, 300 MHz)
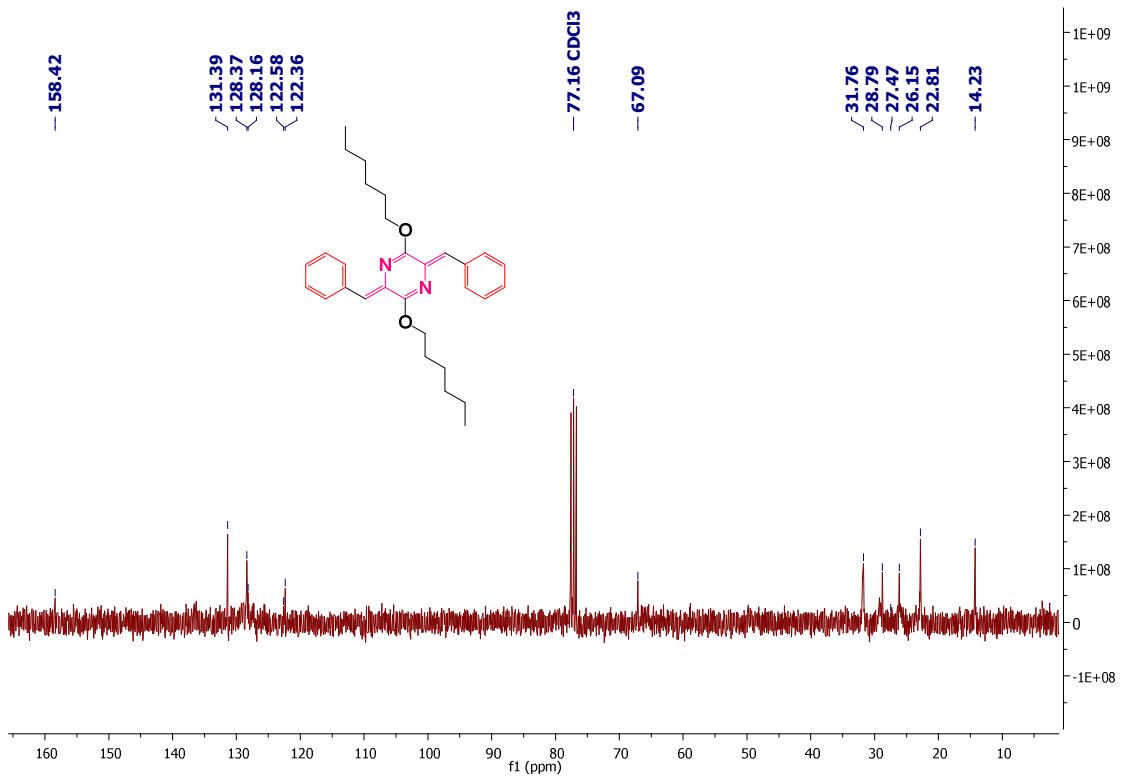
Figure S19: ^{13}C NMR spectrum of **AQM1** (CDCl$_3$, 75 MHz)
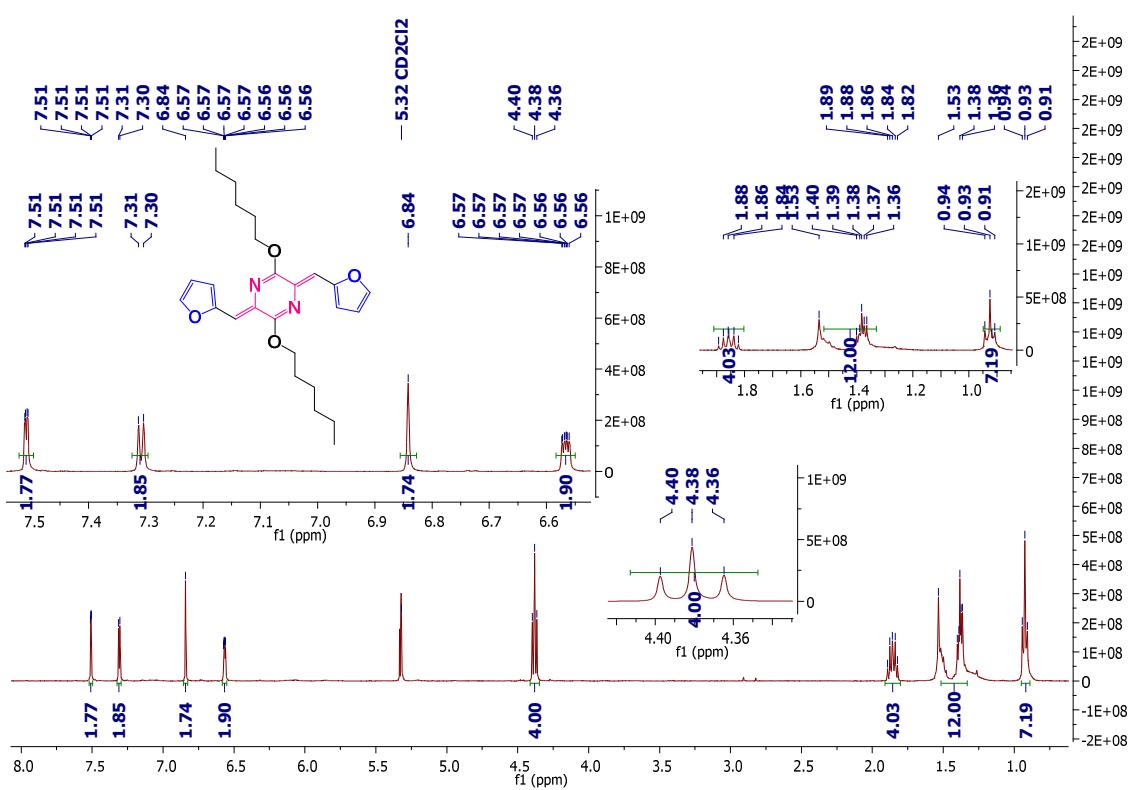
Figure S20: ^{1}H NMR spectrum of **AQM2** (CD$_2$Cl$_2$, 400 MHz)
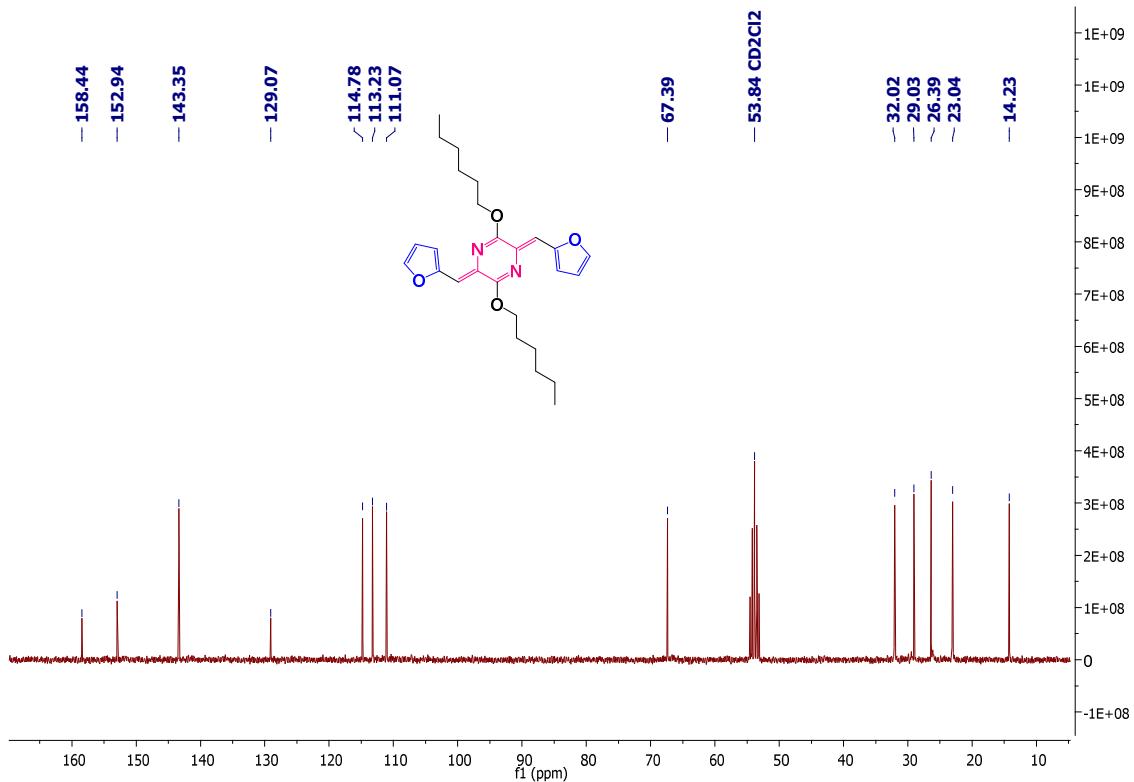
Figure S21: ^{13}C NMR spectrum of **AQM2** (CD$_2$Cl$_2$, 75 MHz)
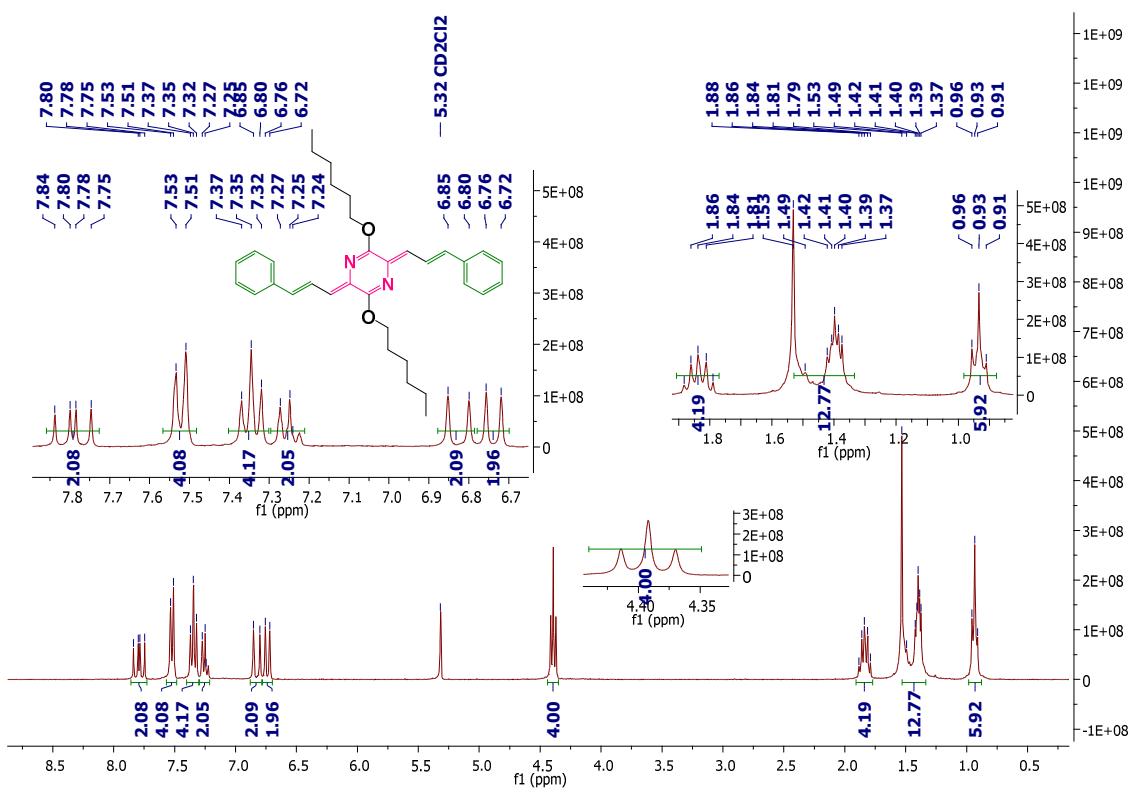
Figure S22: ^{1}H NMR spectrum of **AQM3** (CD$_2$Cl$_2$, 300 MHz)
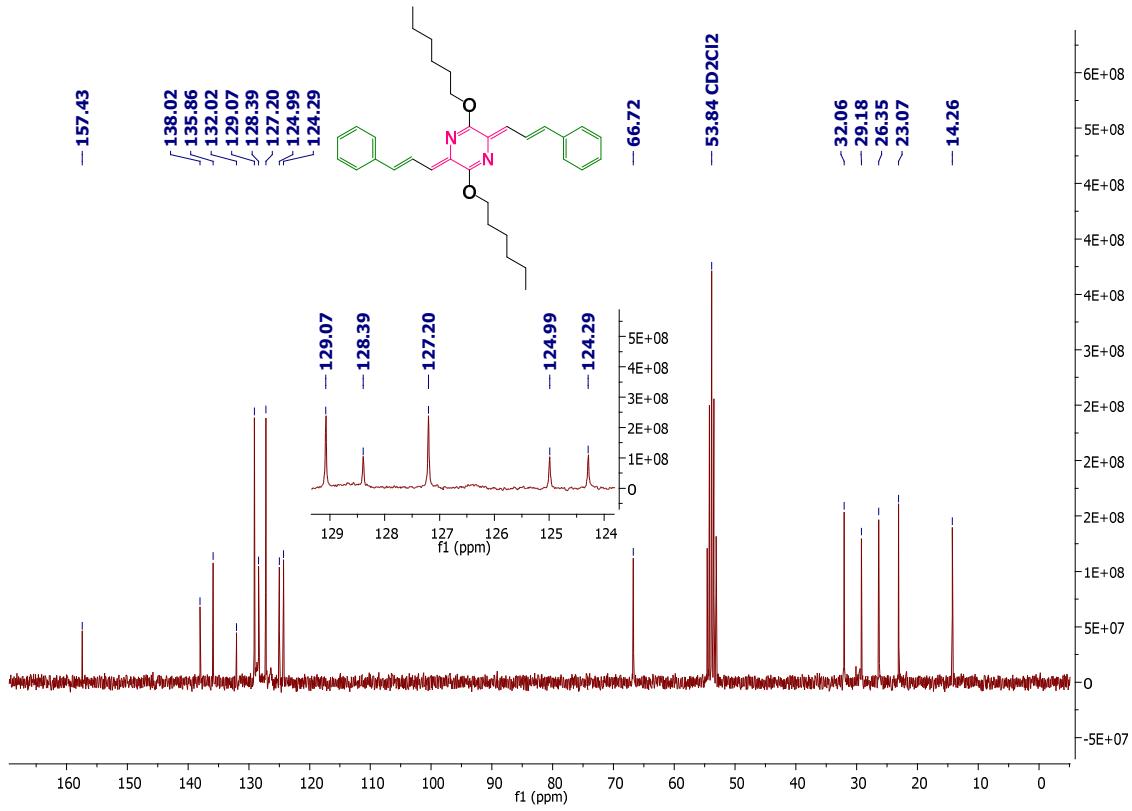
Figure S23: ^{13}C NMR spectrum of **AQM3** (CD$_2$Cl$_2$, 75 MHz)

References

(1) Reiss, H.; Heller, A. The Absolute Potential of the Standard Hydrogen Electrode: A New Estimate. *J. Phys. Chem.* **1985**, *89* (20), 4207–4213. https://doi.org/10.1021/j100266a013.