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An Iminodibenzyl-Quinoxaline-Iminodibenzyl Scaffold as a Mechanochromic and Dual Emitter: Donor and Bridge Effects on Optical Properties

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1. General methods:

^{1}H and ^{13}C NMR spectroscopy was carried out on a Bruker Avance 400 NMR spectrometer at 400 MHz and 100 MHz, respectively; δ in ppm. The residue signals of the solvents were used as internal standards. Attenuated total reflection infrared (ATR IR) spectra were recorded using a Bruker VERTEX 70 spectrometer. MS data was recorded on UPLC-MS Acquity Waters SQ Detector 2.

Absorption spectra of 10^{-5} M solutions or films were measured with Perkin Elmer Lambda 35 spectrometer or UV-3600 double beam spectrophotometer (Shimadzu). Photoluminescence (PL) spectra of 10^{-5} M solutions, films, and powders were recorded using Edinburgh Instruments' FLS980 Fluorescence Spectrometer or FluoroMax-3 fluorescence spectrometer (Jobin Yvon). Phosphorescence, prompt fluorescence (PF), and delayed fluorescence (DF) spectra and fluorescence decay curves were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using either third harmonics of a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or a N_2 laser emitting at 337 nm. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/DF time resolved measurements were performed by exponentially increasing gate and integration times. Temperature-dependent experiments were conducted using a continuous flow liquid nitrogen cryostat (Janis Research) under nitrogen atmosphere, while measurements at room temperature were recorded in vacuum in the same cryostat. Photoluminescence quantum yield has been recorded using Fluorescein in 0.1 M NaOH as a standard (Φ = 0.90). Power dependence data was fitted using a linear espression: $y = a \cdot x$ for linear relation.

The single crystals of compounds were obtained from the mixture of solvents (DCM, acetone, hexane). Yellow color single crystals were mounted on the glass capillary using glue. The crystallographic analysis was performed employing XtaLAB mini diffractometer (Rigaku) with graphite monochromated Mo Kα (λ=0.71075 Å) X-ray source. The measurements were performed at the temperature of 293 K.

Thermogravimetric analysis (TGA) was performed on a Metter TGA/SDTA851e/LF/1100 apparatus at a heating rate of 20°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were done on a DSC Q 100 TA Instrument at a heating rate of 10°C/min under nitrogen atmosphere

Cyclic voltammetry (CV) measurements were carried out with Eco Chemie Company's AUTOLAB potentiostat "PGSTAT20" and a glassy carbon working electrode in a three electrode cell. The measurements were performed in 0.1 M nBu_4NPF_6 solution in anhydrous dichloromethane at room temperature under nitrogen atmosphere.

The crystallographic nature of the powder materials was determined using D8 Discover X-ray diffractometer (Bruker AXS GmbH) with Cu Kα (λ= 1.54 Å) X-ray source. Parallel beam geometry with 60 mm Göbel mirror (i.e. X-ray mirror on a high precision parabolic surface) was used. This configuration enables transforming the divergent incident X-ray beam from a line focus of the X-ray tube into a parallel beam that is free of Kβ radiation. Primary side also had a Soller slit with an axial divergence of 2.5 º and a slit of 1 mm. The secondary side had a LYNXEYE (1D mode) detector with an opening angle of 2.160 º and slit opening of 6.0 mm. X-ray generator voltage and current was 40.0 kV and 40 mA, respectively. Coupled 2θ/θ scans were performed in the range of 3.0-60.0 º with a step size of 0.028 º, time per step of 19.2 s and auto-repeat function enabled. Processing of the resultant diffractograms was performed with DIFFRAC.EVA software.

2. Synthetic procedure:

1,2-dicholoro quinoxaline (I), 2,3-bis(4-bromophenyl)quinoxaline (V) and 2,8-dibromo-5*H*-dibenzo[*b,f*]azepine are prepared by the reported method in the literature.[1-3]

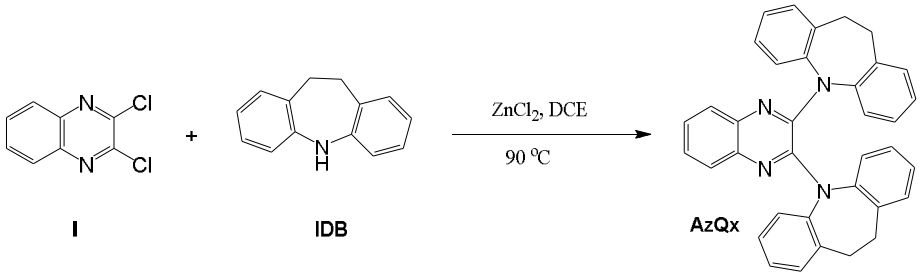


Figure S1: Synthetic procedure for preparation of AzQx

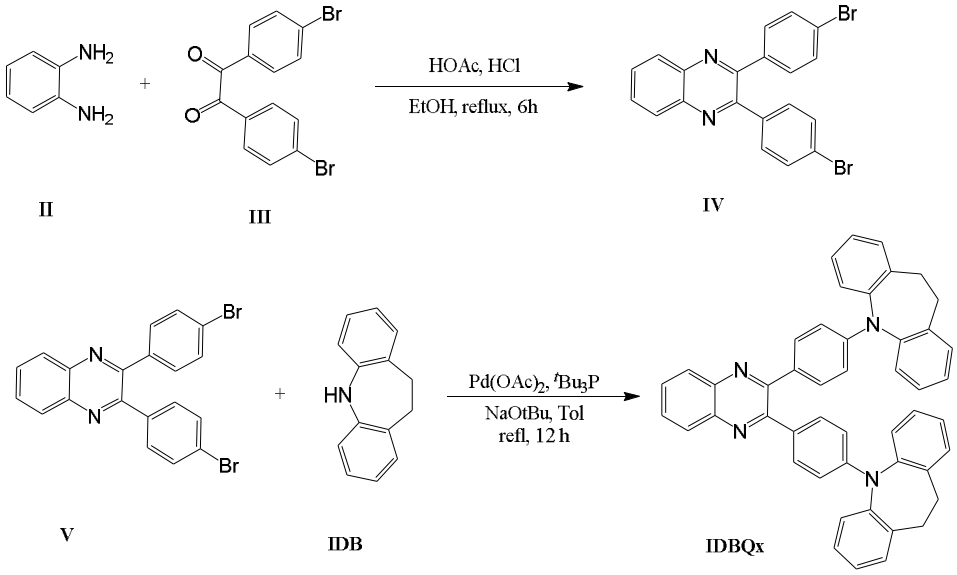


Figure S2: Synthesis routes for preparation of IDBQx

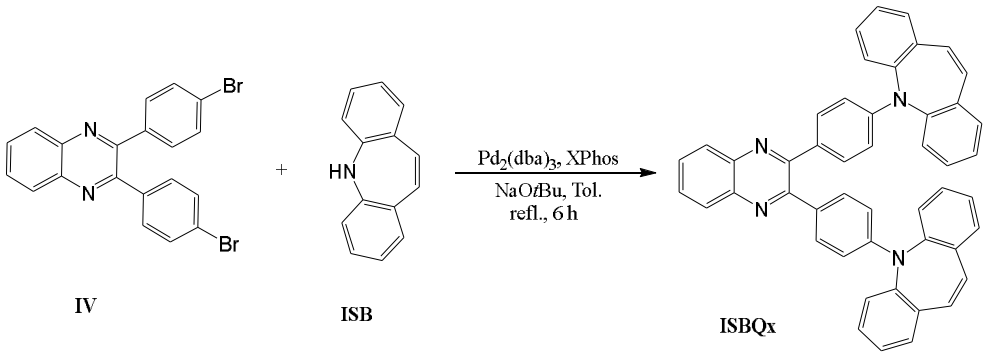


Figure S3: Synthesis procedure to generate ISBQx

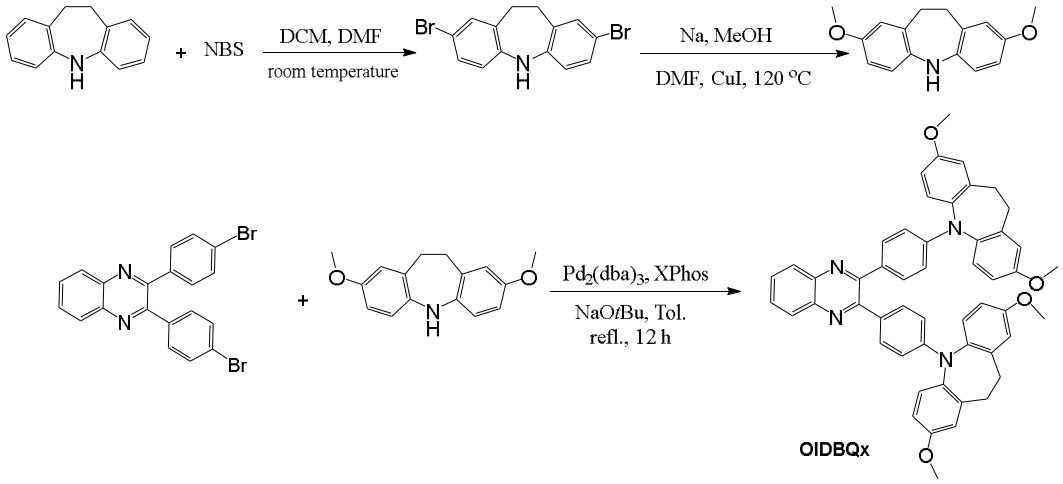
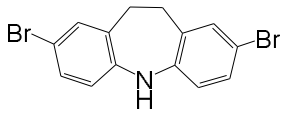


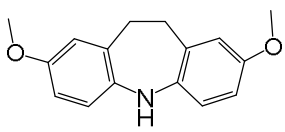
Figure S4: Synthesis routs for generation of OIDBQx

Synthesis of 2,8-dibromo-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine:



Iminodibenzyl (5 mmol) was added to a solution of DCM (15 mL) in silica gel (2 g). After stirring for 5min *N*-bromosuccinimide (NBS, 10 mmol, 1.78 g) dissolved in DCM:DMF (25:15 mL) was added dropwise and stirred for 1 h at room temperature. Reaction mixture filtered and washed with DCM. The crude product were purified by column chromatography (n-hexane/EtOAc 10:1) to give the white powder. Yield (1.10 g, 63%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 8.58 (1H, s, NH), 7.2 (2H, s, CH), 7.19 (2H, d, ^{3}J= 9.4 Hz, CH), 6.91 (2H, d, ^{3}J= 9.2 Hz, CH), 2.92 (4H, s, CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 142.2, 132.8, 130.6, 129.6, 120.4, 110.1, 34.5 ppm. MS, m/z = 350 ([M-H]$^+$, 36%) 353 ([M+2, 100%]$^+$).

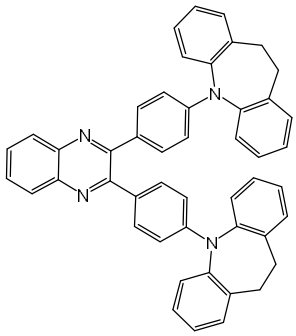
Synthesis of 2,8-dimethoxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine:



Na (3.2 g) was dissolved in dry MeOH (25 mL) under N_2 at 0 °C, and then 2,8-dibromo-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine (1.1 g, 3.1 mmol), CuI (1.18 g, 6.2 mmol) and DMF (30 mL) at 125 °C for 12 h were stirred. After cooling to room temperature, the mixture was filtered through silica gel with EtOAc, and evaporated and washed with water and dried over Na_2SO_4. The combined organic layers were purified by

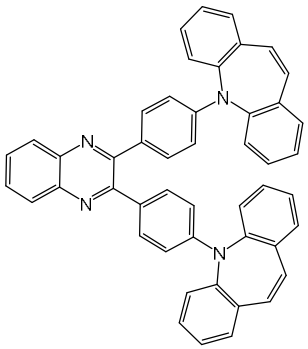
column chromatography on silica gel (n-Hexane/EtOAc 6:1) to afford the white product. Yield (616 mg, 78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 7.66 (1H, s, NH), 6.85 (2H, d, ^{3}J= 8.6 Hz, CH), 6.64-6.59 (4H, m, CH), 3.66 (6H, s, OMe), 2.92 (4H, s, CH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C = 152.2, 138.0, 129.0, 119.1, 115.6, 112.8, 55.6, 34.7 ppm. MS, m/z = 254 ([M]$^+$, 100%). HRMS (ESI): calcd for $C_{16}H_{17}NO_2$ ([M+H]$^+$): 255.1259; found: 255.1253.

Synthesis of 2,3-bis(4-(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)phenyl)quinoxaline (IDBQx):



Procedure A: Two neck flask was charged with Iminodibenzyl (468 g, 2.4 mmol), 2,3-bis(4-bromophenyl)quinoxaline (438 mg, 1 mmol) and NaO*t*-Bu (250 mg), evacuated and backfilled with N_2 for 3 times. Then, $Pd(OAc)_2$ (22 mg, 0.01 mmol, 10 mol%) and *t*Bu_3P (25 mg, 0.12 mmol, 12 mol%) were added under flow on nitrogen, and followed by charging with 10 mL of toluene. Reaction stirred for overnight at reflux. After cooling to room temperature, the mixture was filtered through silica gel by $CHCl_3$, and concentrated in vacuum. The crude product were isolated by column chromatography on silica gel (n-hexane/EtOAc 4:1) to afford yellow powder. Yield (454 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.98 (2H, dd, ^{3}J= 6.1 Hz, ^{4}J= 3.3 Hz, CH), 7.54 (2H, dd, ^{3}J= 6.4 Hz, ^{4}J= 3.4 Hz, CH), 7.34 (4H, d, ^{4}J= 7.6 Hz, CH), 7.25 (4H, d, ^{3}J= 8.8 Hz, CH), 7.20-7.12 (12H, m, CH), 6.44 (4H, d, ^{3}J= 8.8 Hz, CH), 2.89 (8H, s, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 153.4, 149.6, 143.2, 140.7, 138.2, 130.9, 130.6, 129.9, 129.0, 128.7, 127.3, 127.1, 112.3, 30.7 ppm. MS, m/z = 668 ([M]$^+$, 19%), HRMS (ESI) calcd for $C_{48}H_{36}N_4$ ([M+H]$^+$): 669.3013; found: 669.3013.

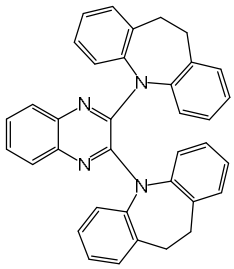
Synthesis of 2,3-bis(4-(5*H*-dibenzo[*b,f*]azepin-5-yl)phenyl)quinoxaline (ISBQx):



Procedure B: Two neck flask was charged with iminostilbene (340 mg, 1.76 mmol), 2,3-bis(4-bromophenyl)quinoxaline (365 mg, 0.83 mmol) and NaO*t*-Bu (354 mg, 3.8 mmol), evacuated and backfilled with N_2 for 3 times. Then, $Pd_2(dba)_3$ (56 mg, 0.06 mmol, 7 mol%) and XPhos (40 mg, 0.08 mmol, 10 mol%) were added under flow on nitrogen, and followed by charging with 10 mL of toluene. Reaction stirred for 6 hours at reflux. After cooling to room temperature, the mixture was filtered through silica gel by $CHCl_3$, and concentrated in vacuum. The crude product were isolated by column chromatography on silica gel (n-hexane/EtOAc 5:1) to afford yellow powder. Yield (402 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.96 (2H, bs, CH), 7.54 (2H, dd, ^{3}J= 6.3 Hz, ^{4}J= 3.0 Hz, CH), 7.43 (2H, dd, ^{4}J= 3.8 Hz, CH), 7.36 (4H, d, ^{3}J= 7.6 Hz, CH), 7.32-7.28 (4H, m, CH), 7.13 (4H, d, ^{3}J= 8.8 Hz, CH), 6.70 (4H, s, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 153.1, 149.5, 142.7, 140.3, 136.2, 130.5, 130.3, 130.2, 130.1, 129.7, 129.1, 128.4, 127.2, 111.8 ppm. MS, m/z = 664 ([M]$^+$, 48%). HRMS (ESI) calcd for $C_{48}H_{32}N_4$ ([M+H]$^+$): 665.2700; found: 665.2706.

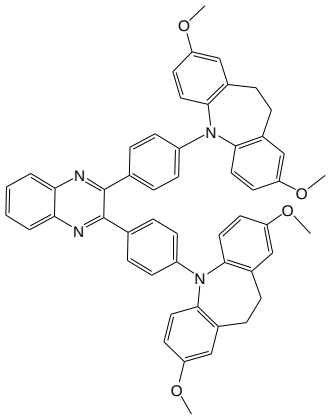
Synthesis of 2,3-bis(10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)quinoxaline (AzQx):

Due to twist boat conformation of IDB in this small molecule desymmetrization resulted in exhibiting 18 carbon peaks in ^{13}CNMR.



A mixture of iminodibenzyl (410 mg, 2.1 mmol) and 2,3-dichloroquinoxaline (198 mg, 1 mmol) dissolved in 7 mL DCE and and added $ZnCl_2$ (286 mg, 2.1 mmol) at 90 ^oC for 12 h. After completion, the reaction mixture was poured into 30 mL water, and organic products were extracted with DCM (3x15mL). The crude compound was purified by column chromatography (n-hexane/DCM 1:1) to afford yellow powder. Yield (93 mg, 18%). ^1H NMR (400 MHz, $CDCl_3$): δ_H = 8.03 (2H, dd, ^3J= 6.3 Hz, ^4J= 3.4 Hz, 2CH), 7.61 (2H, dd, ^3J= 6.3 Hz, ^4J= 3.4 Hz, 2CH), 7.35 (2H, d, ^4J= 2.1 Hz, CH), 7.09 (2H, dd, ^3J= 8.3 Hz, ^4J= 2.1 Hz, CH), 7.03-6.96 (4H, m, CH), 6.07 (2H, t, ^3J= 7.4 Hz, CH), 6.67 (2H, d, ^3J= 8.3 Hz, CH), 6.54 (2H, d, ^3J= 8.3 Hz, CH), 6.06 (2H, s, CH), 2.99 (8H, s, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 153.0, 142.9, 141.8, 140.9, 132.3, 130.6, 130.0, 129.2, 129.0, 128.8, 128.6, 128.0, 126.9, 119.9, 118.1, 117.4, 35.2, 34.9 ppm. MS, m/z = 516 ([M]$^+$, 51%). HRMS (ESI)) calcd for $C_{36}H_{282}N_4$ ([M+H]$^+$): 517.2387; found: 517.2390.

Synthesis of 2,3-bis(4-(2,8-dimethoxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepin-5-yl)phenyl)quinoxaline (OIDBQx):



Prepared according to the procedure B, and organic products were extracted with DCM. The crude product was purified by column chromatography (n-hexane/DCM 1:1). Yield (490 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ_H = 7.95 (2H, dd, ^3J= 6.3 Hz, ^4J= 3.4 Hz, CH), 7.54 (2H, dd, ^3J= 6.3 Hz, ^4J= 3.4 Hz, CH), 7.25-7.21 (8H, m, CH), 6.73-6.70 (8H, m, CH), 6.40 (4H, d, ^3J= 8.9 Hz, CH), 3.72(12H, s, OMe), 2.84 (8H, s, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 158.3, 153.5, 150.4, 140.8, 139.3, 136.7, 130.7, 130.5, 128.8, 128.4, 115.6, 112.4, 112.2, 55.4, 30.9 ppm. MS, m/z = 788 ([M]$^+$, 1%). HRMS (ESI) calcd for $C_{52}H_{44}N_4O_4$ ([M+H]$^+$): 789.3435; found: 789.3440.

3. Electrochemical characterization:

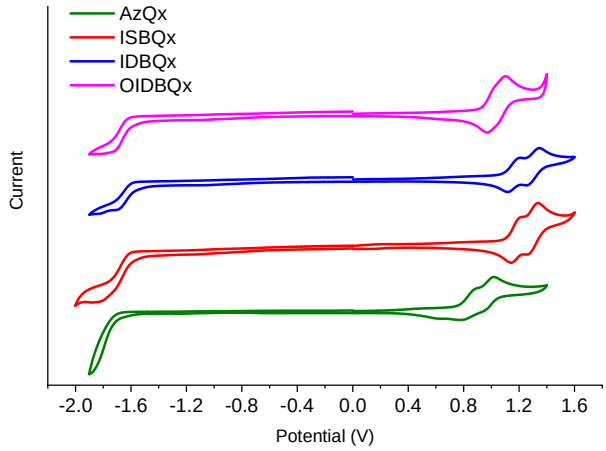


Figure S5. Oxidation and reduction potential of compounds in DCM recorded with cyclic voltammetry.

E_{HOMO} = - ($E^{1/0}{}_{1/2}$ (vs. Fc^+/Fc) +4.8), E_{LUMO} = - ($E^{0/1}$ (vs. Fc^+/Fc) + 4.8)

4. DSC and TGA Analyses:

Molecules with phenylene linkage demonstrated higher thermal stability and glass transition than AzQx. These desired behaviours can be ascribed to increasing of intermolecular interactions. In addition, AzQx did not show any melting point and attributed to its amorphous form.

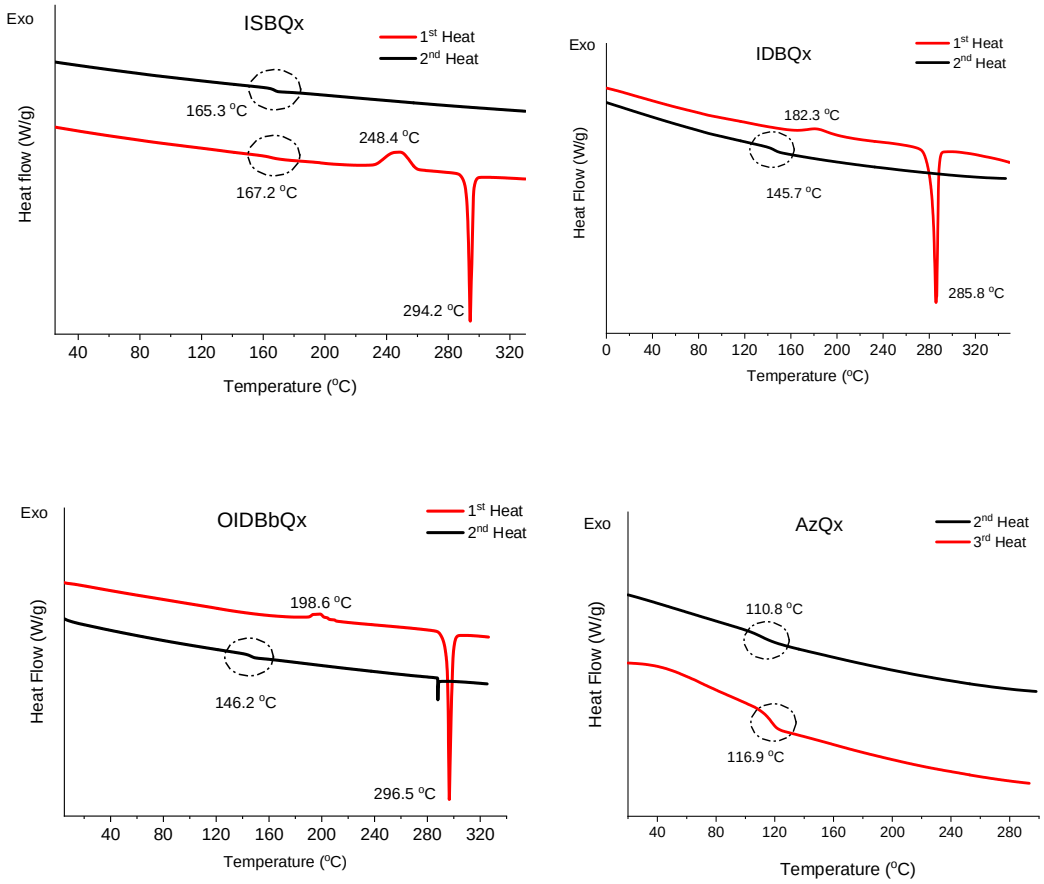


Figure S6. Differential scanning calomery analysis of samples.

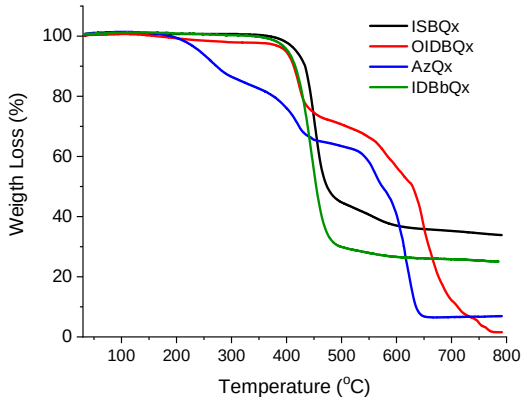


Figure S7. The TGA thermograms of materials (5% weight loss).

5. Photophysical characterization:

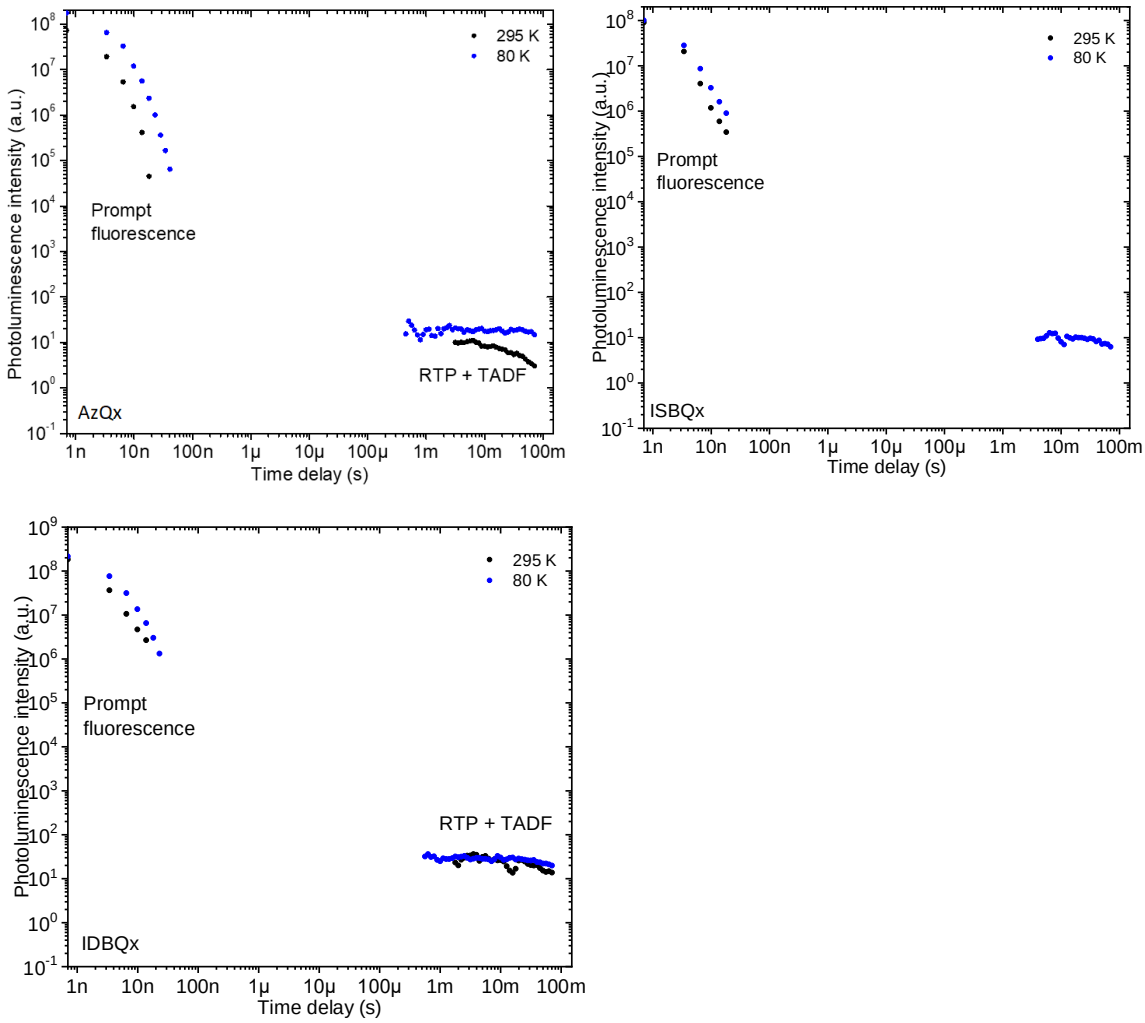


Figure S8. Photoluminescence decay transients at 80 and 295 K in Zeonex.

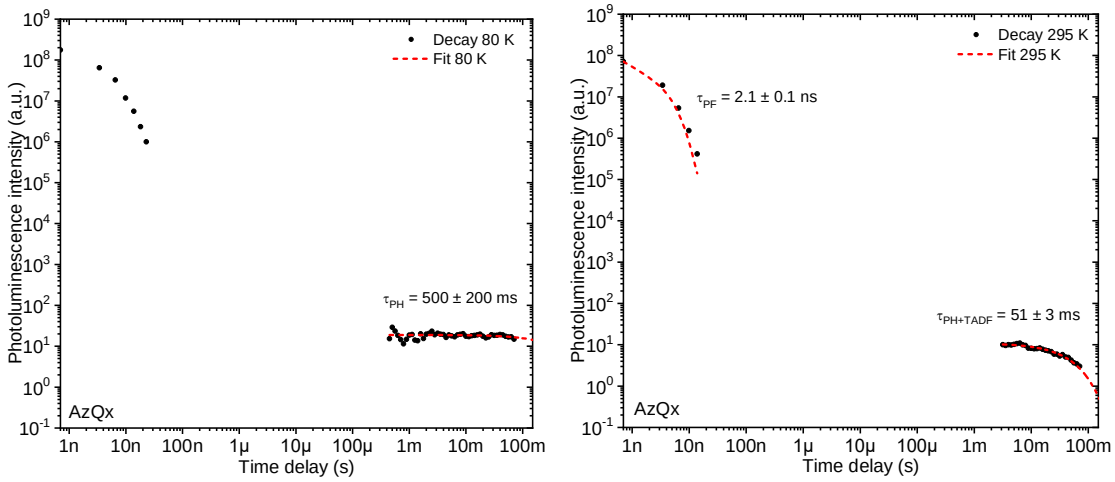


Figure S9. Photoluminescence decay transient fits of AzQx at 80 and 295 K in Zeonex.

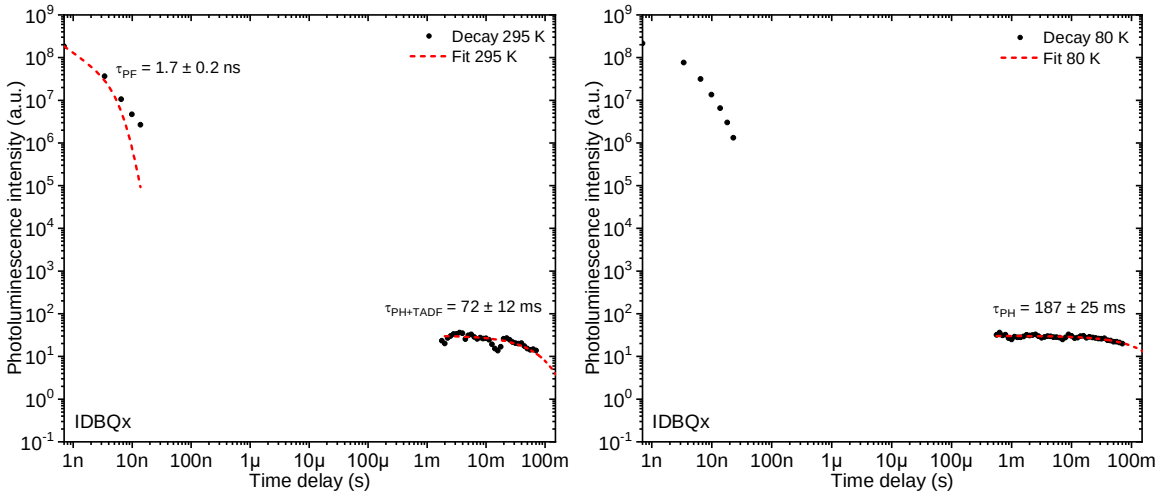


Figure S10. Photoluminescence decay transient fits of IDBQx at 80 and 295 K in Zeonex.

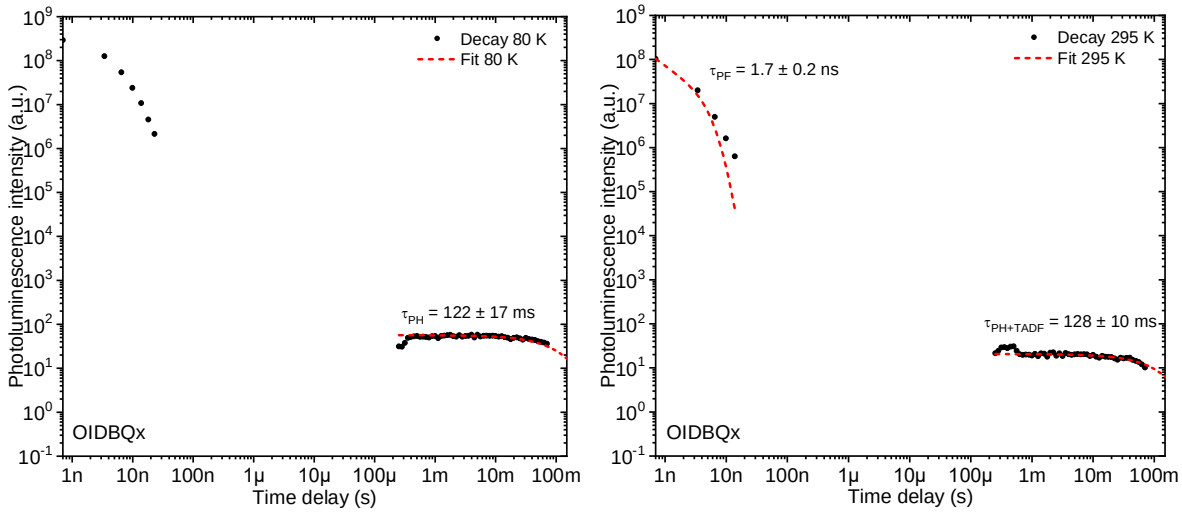


Figure S11. Photoluminescence decay transient fits of OIDBQx at 80 and 295 K in Zeonex.

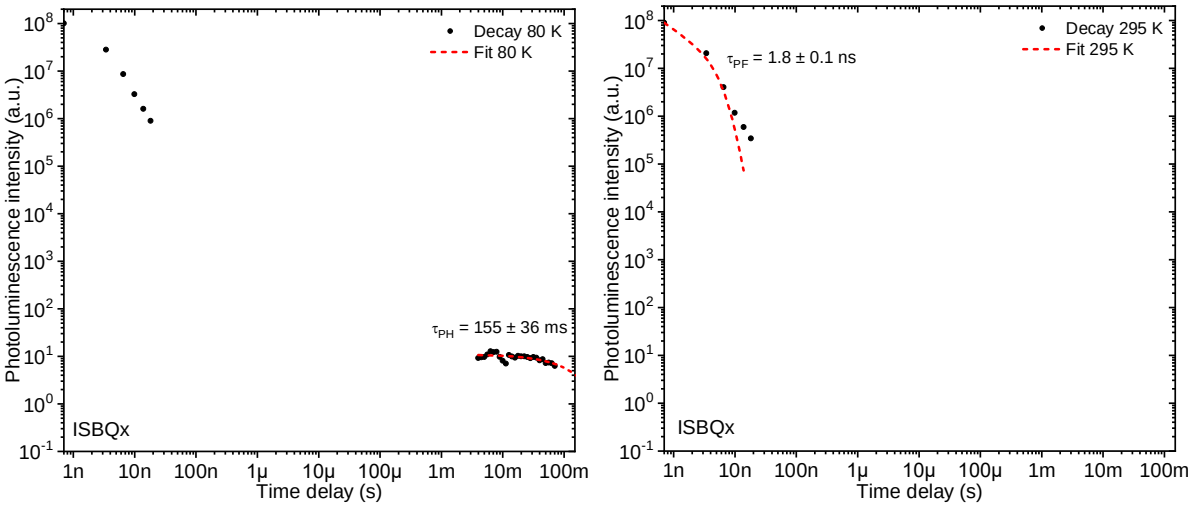


Figure S12. Photoluminescence decay transient fits of ISBQx at 80 and 295 K in Zeonex.

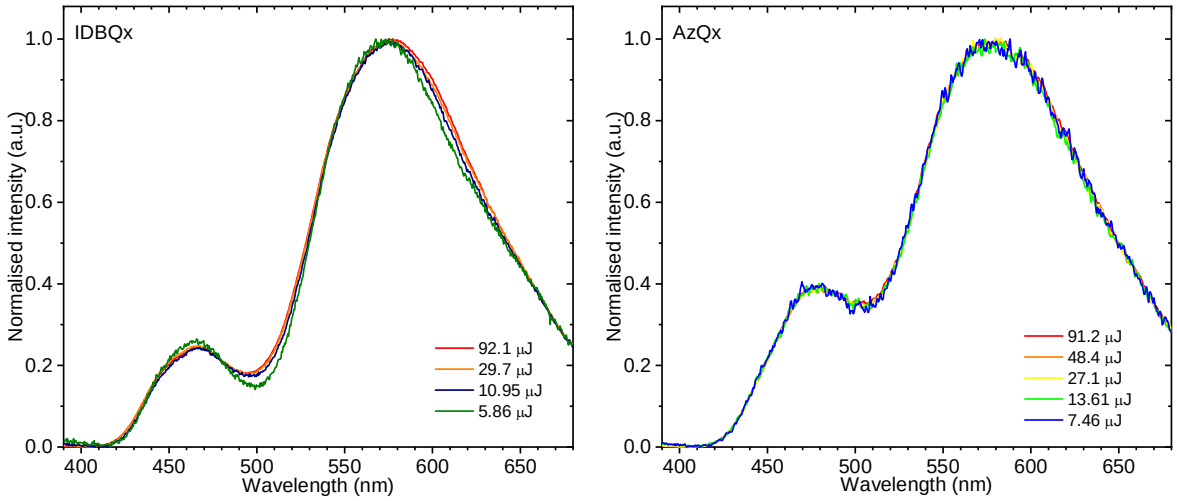


Figure S13. Delayed fluorescence and room temperature phosphorescence spectra at 295 K recorded with various excitation pulse energy.

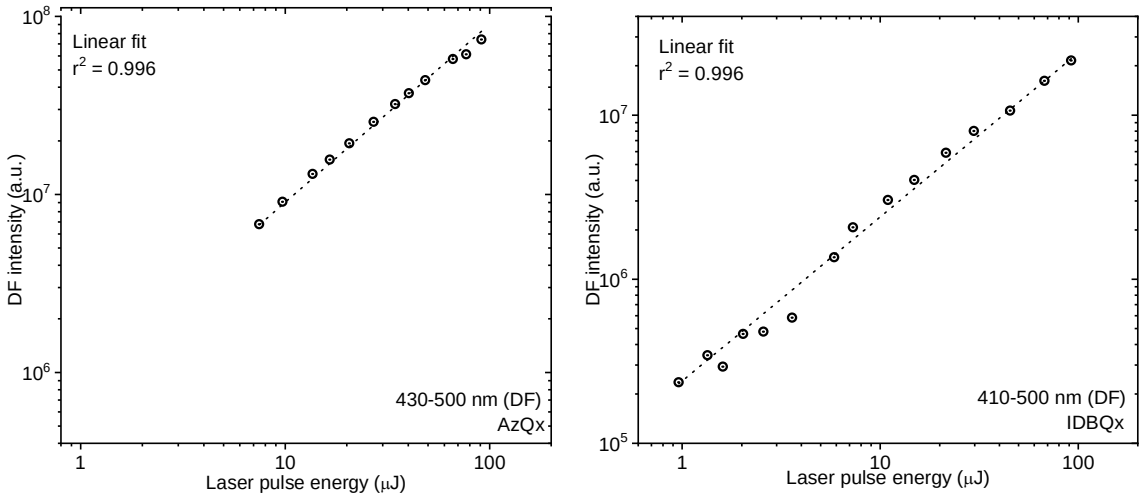


Figure S14. Laser fluence dependence of delayed fluorescence at room temperature in Zeonex.

6. Mechanochromic characteristics

Table S1 PL and decay time of OIDBQx under external stimuli

Sample (OIDBQx)	Initial	Ground	Fumed	Neat film
PL (nm)	494	522	495	518
τ_1 (ns)	0.21 (46.41%)	1.40 (70.83%)	0.32 (60.81%)	1.39 (72.86%)
τ_2 (ns)	1.67 (53.59%)	4.48 (29.15%)	1.72 (39.19%)	4.30 (27.14%)
X^2	1.07	1.06	1.07	1.03

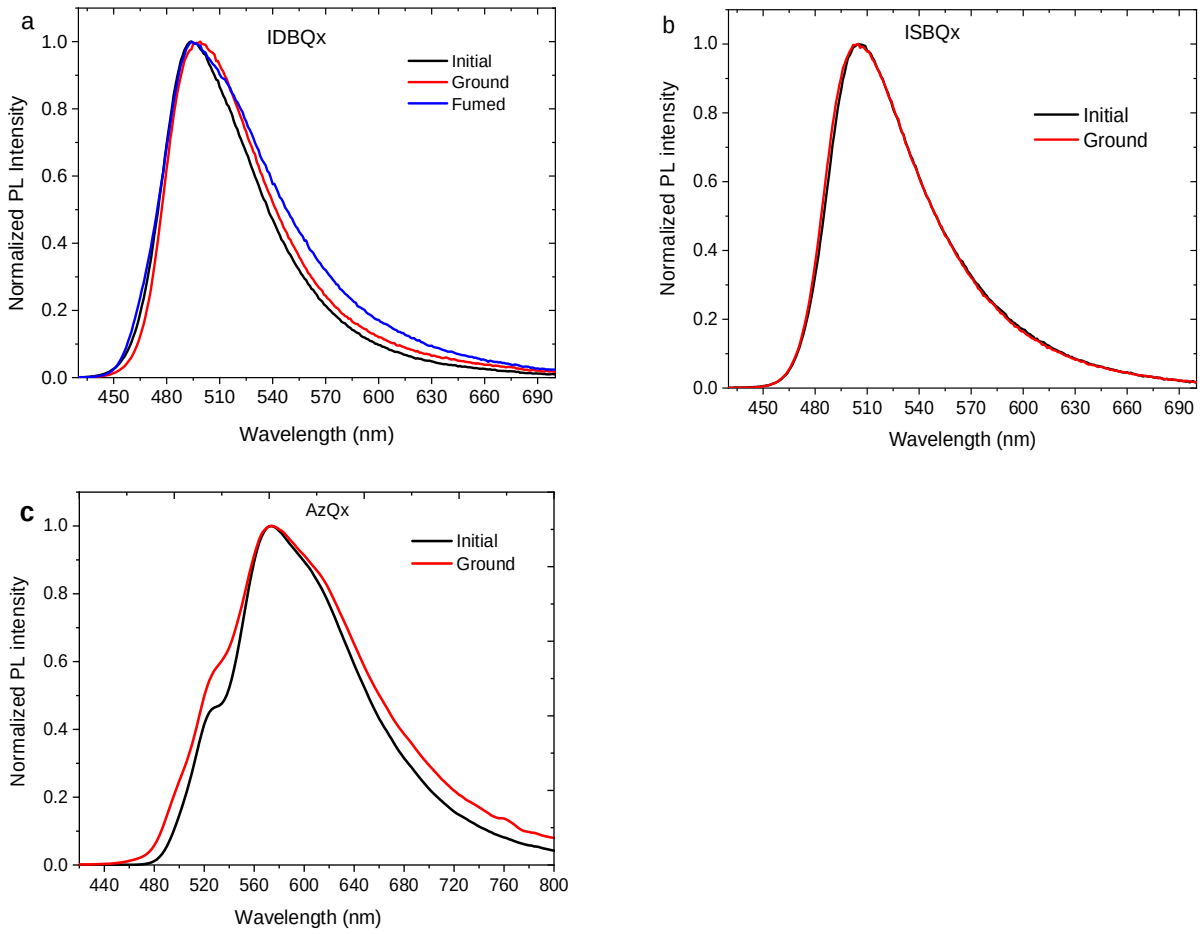


Figure S15. PL spectra of a) IDBQx and b) ISBQx and c) AzQx under external stimuli.

7. Powder XRD analyses:

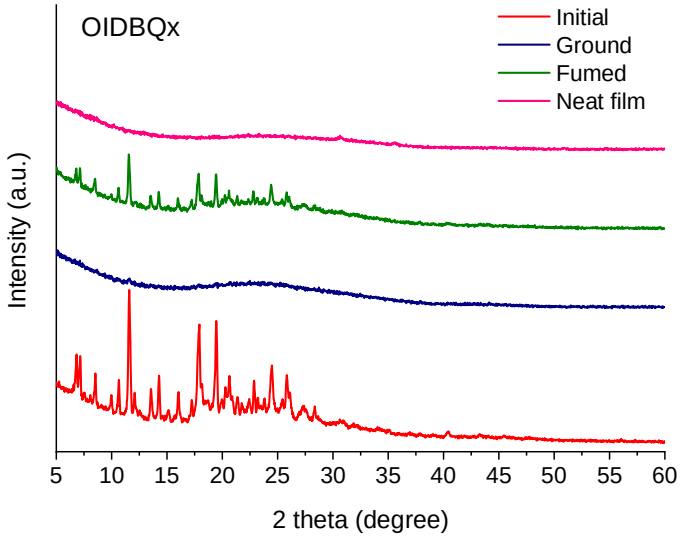


Figure S16. Powder Xray diffractogram of OIDBQx under application in initial form (-i), ground (-g), drop-cast film (-df) and after fumigation (-f).

8. Single crystal XRD analyses:

The crystallographic data is summarized in Table S2. Packing along a-axis is presented in Figure S15 and S16. The crystallographic data for structures IDBQx and ISBQx reported in this paper have been deposited in Cambridge Crystallographic Data Centre with CCDC no 1861441-1861442. The copies of data can be obtained free of charge on application to CCDC.(The Cambridge Structural Database (CSD)- The Cambridge Crystallographic Data Centre (CCDC), (http://www.ccdc.cam.ac.uk/solutions/csd-system/components/csd/). Calculations/visualizations were performed using the OLEX2 crystallographic software[3] package except for refinement, which was performed using SHELXL. [4,5] For molecule ISBQx solvent mask procedure was used. Anisotropic thermal parameters were assigned to all nonhydrogen atoms. The hydrogens were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically.

Table S2. Structure data of IDBQx and ISBQx

	IDBQx	ISBQx
Empirical Formula	$C_{48}H_{36}N_4$. CH_3COCH_3	$C_{48}H_{32}N_4$
Crystal Dimensions (mm)	0.6x0.2x0.2	0.2x0.1x0.1
Crystal System	triclinic	triclinic
Space group	P-1	P-1
Cell angles (°)	α= 102.079(9) β= 93.931(9) γ= 93.152(9)	α= 78.98(2) β= 81.21(2) γ= 67.65(3)
Cell length (Å)	*a* =11.1633(11) *b* =12.2381(14) *c* =15.3155(16)	*a* = 12.135(4) *b* = 12.225(3) *c* = 17.067(4)
Cell volume ($Å^3$)	2036.1(4)	2289.4(12)
Z value	9	10
D_{calc} (g cm^{-3})	1.186	0.964
F (000)	768	696
λ (Mo *K*α) (Å)	0.71073	0.71073
h_{max}, k_{max}, l_{max}	12, 15, 18	14, 12, 21
Temperature (K)	293(2)	293(2)

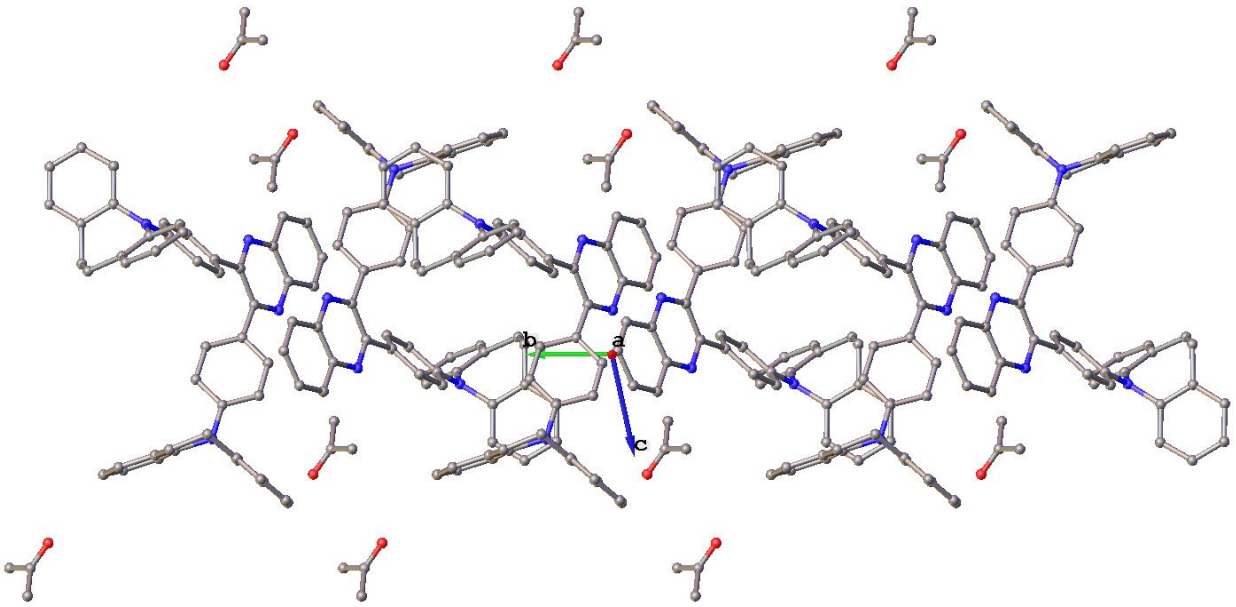


Figure S17. Packing in the crystal structure of compound IDBQx, viewed along the *a*-axis. Hydrogen atoms are removed for clarification

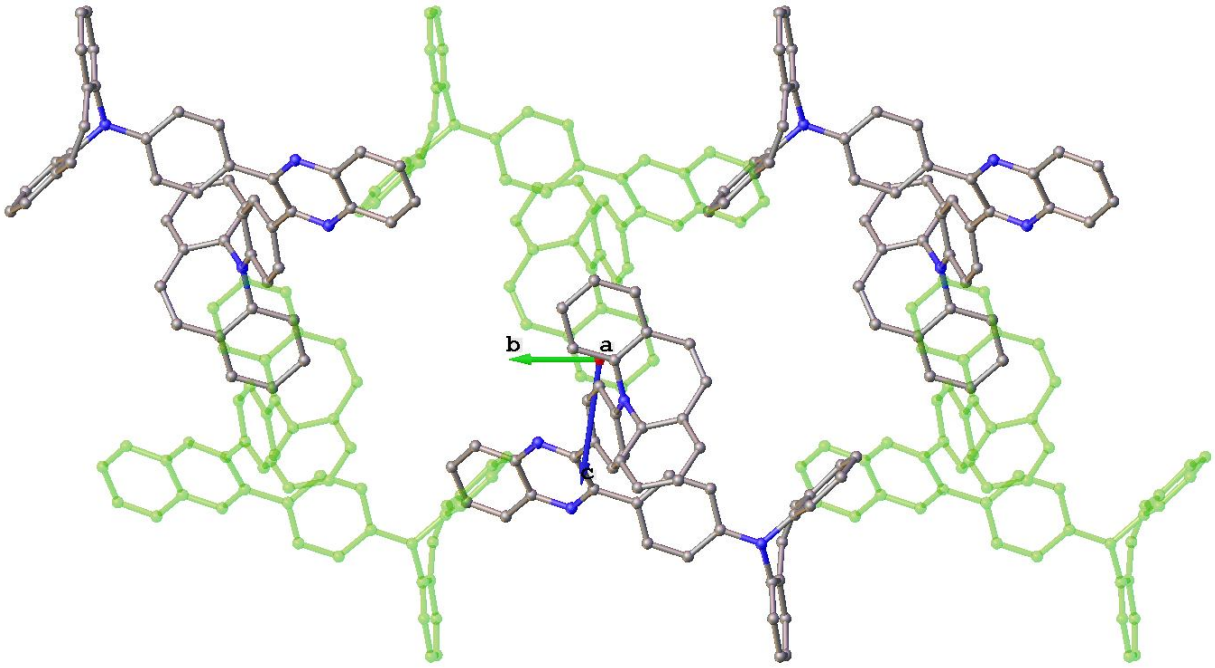


Figure S18. Packing in the crystal structure of compound ISBQx, viewed along the *a*-axis. Molecules have demonstrated with two colors for clarification

References:

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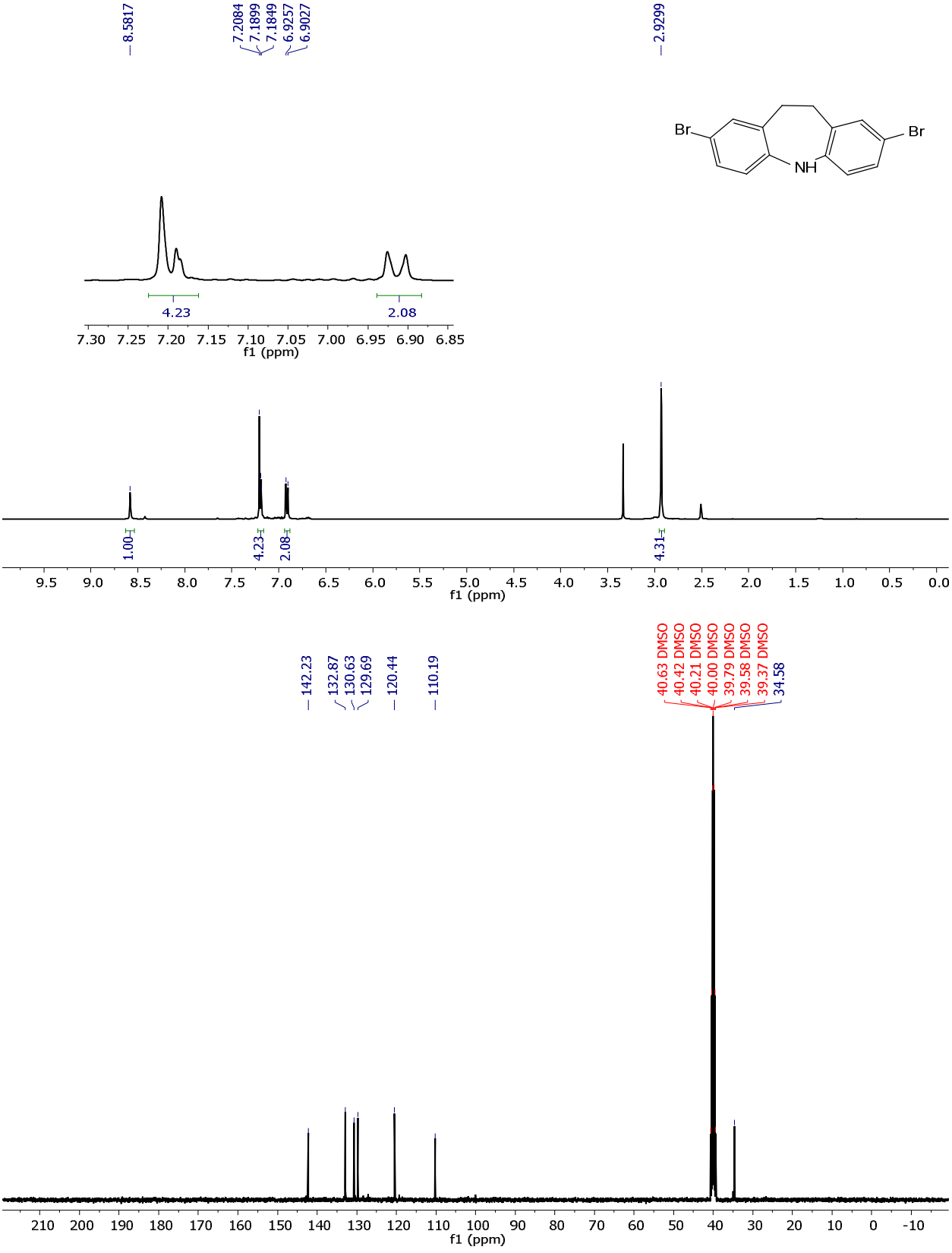
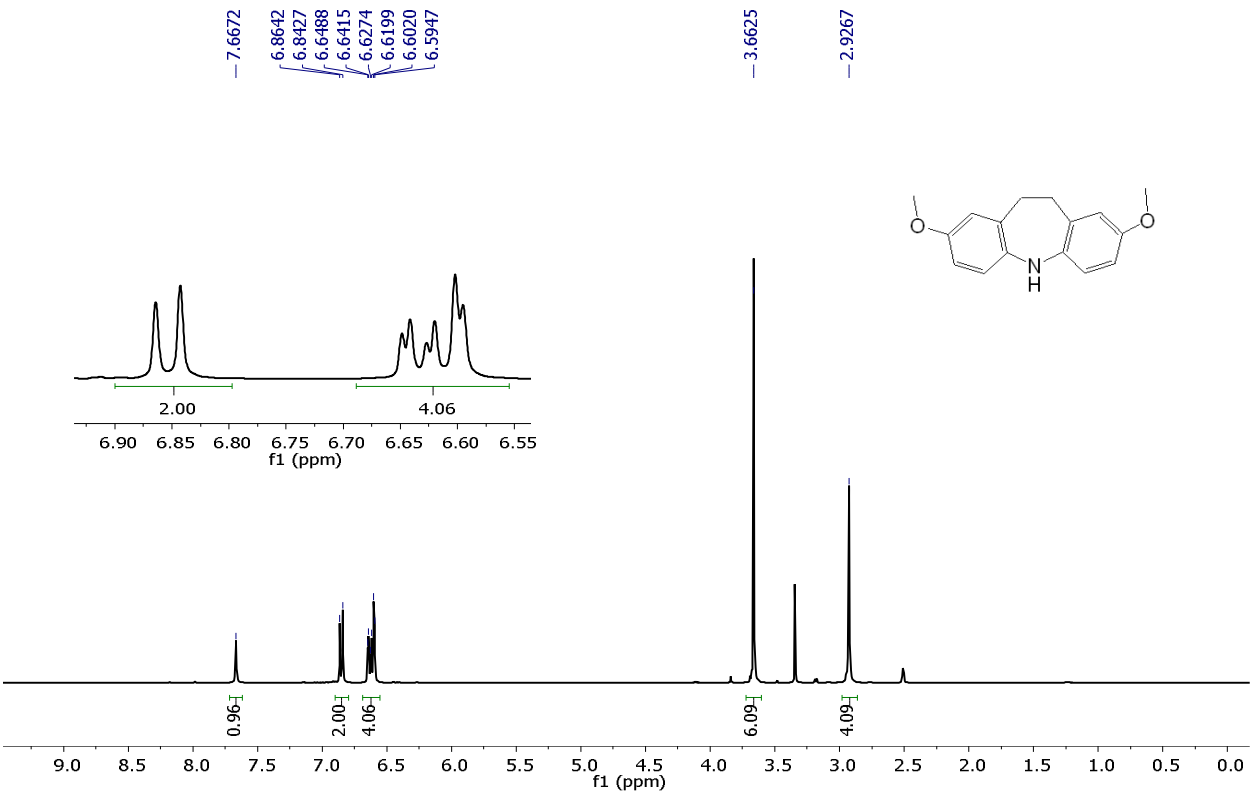
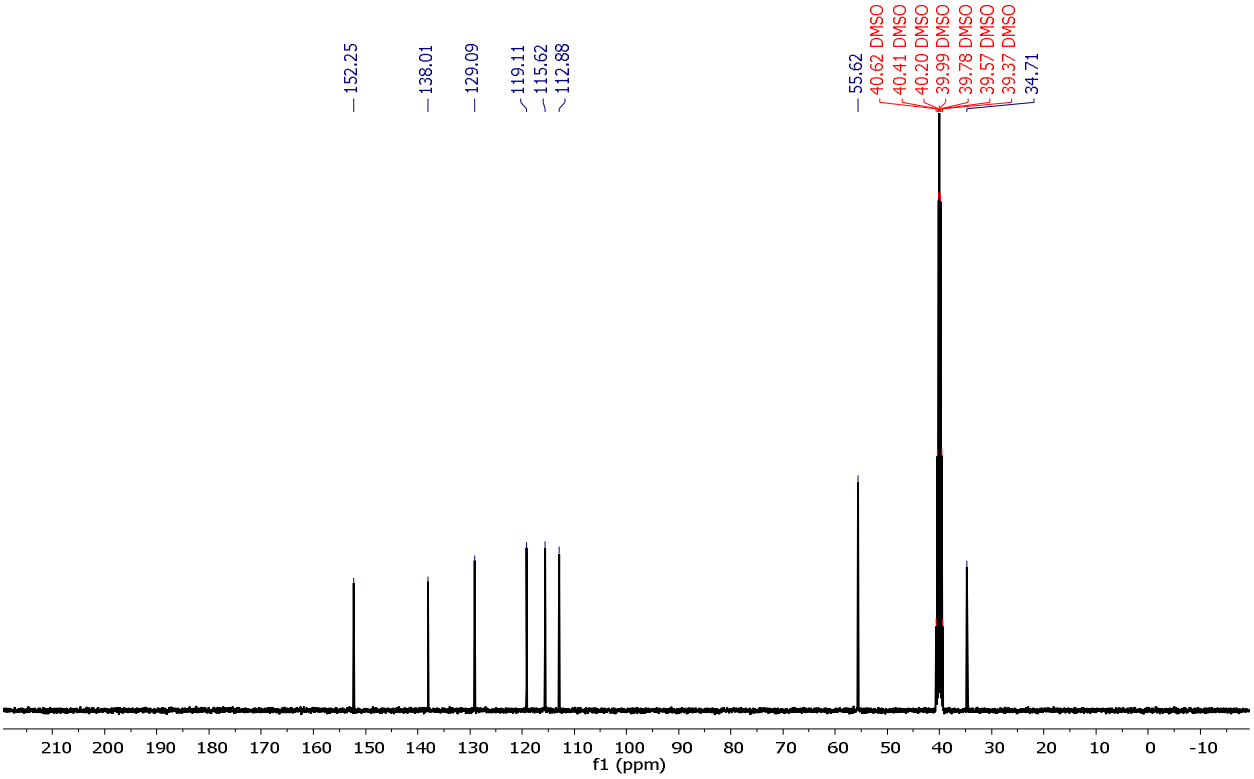
^{1}H and ^{13}C NMR of 2,8-dibromo-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine:

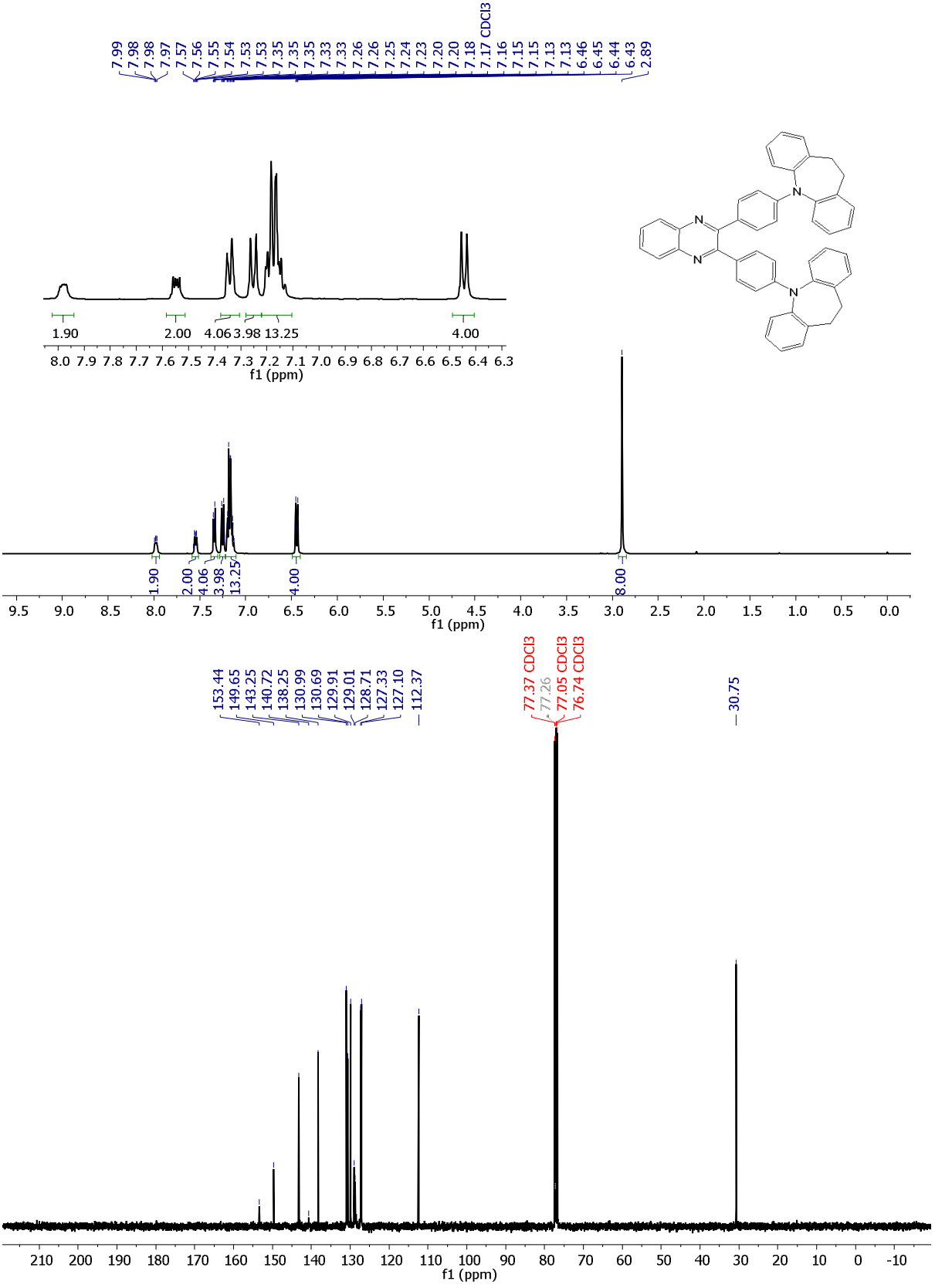


^{1}H and ^{13}C NMR of 2,8-dimethoxy-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine:

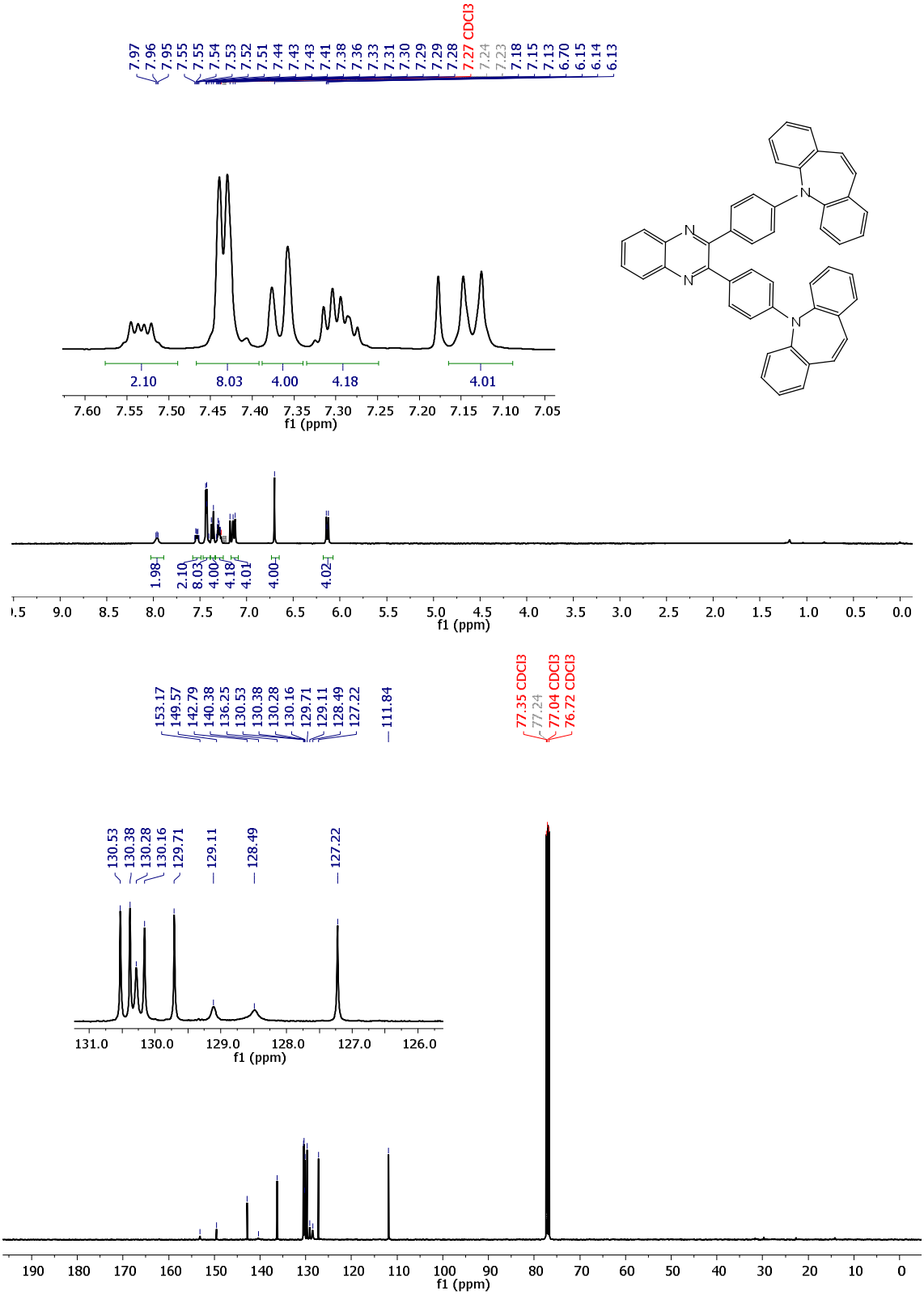




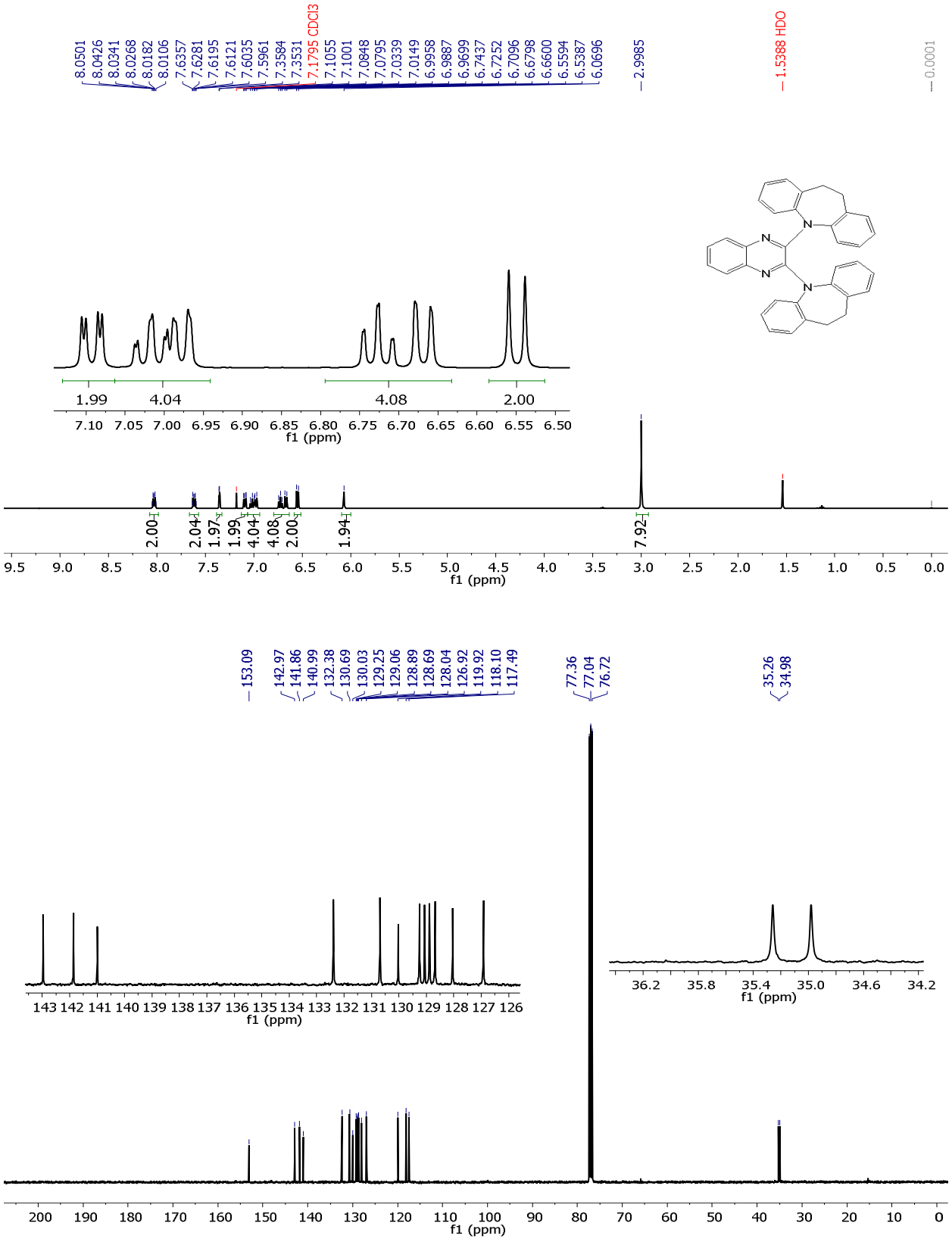
^{1}H and ^{13}C NMR of 2,3-bis(4-(10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)phenyl)quinoxaline (IDBQx):



^{1}H and ^{13}C NMR of 2,3-bis(4-(5*H*-dibenzo[*b*,*f*]azepin-5-yl)phenyl)quinoxaline (ISBQx):



^{1}H and ^{13}C NMR of 2,3-bis(10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)quinoxaline (AzQx):



^{1}H and ^{13}C NMR of 2,3-bis(4-(2,8-dimethoxy-10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)phenyl)quinoxaline (OIDBQx):