Supporting Information for

6MNEP: A molecular cation with large hyperpolarizability and promising for nonlinear optical applications

1. Organic Synthesis and NMR Characterization

6MNEP, MBDM, and DACS compounds were synthesized in a similar manner. Here, we explain the synthesis of 6MENP-T as procedure example.

Methyl 4-methylbenzenesulfonate: Metallic sodium (1.63g, 1eq) was weighed out, washed with hexanes and reacted with dry methanol (80 mL) to produce sodium methoxide. This solution was dropwise added to a 4-methylbenzenesulfonyl chloride/DCM solution (10g in 200 ml of solution) and the solvent evaporated. The resulting solids were extracted with DCM and water, dried over sodium sulfate, and the solvent was removed at reduced pressure. Methyl 4-chlorobenzenesulfonate (83% yield) was obtained and used in the next step without further purification.

1,4-dimethylpyridin-1-ium 4-methylbenzenesulfonate: 4-picoline (12g, 2 eq) was combined with 4-methylbenzenesulfonate (10.5g, 1eq) in toluene. The mixture was stirred at 100°C for 3h, then the precipitated solids were filtered and washed with toluene. A white powder was recovered and identified as 1,4-dimethylpyridin-1-ium 4-methylbenzenesulfonate (98% yield)

(E)-4-(2-(6-methoxynaphthalen-2-yl)vinyl)-1-methylpyridin-1-ium 4-methylbenzenesulfonate (6MNEP-T): 1,4-dimethylpyridin-1-ium 4-chlorobenzenesulfonate (17g, 1eq) was combined with 6-methoxy naphtaldehyde (8.13g, 1eq) in ethanol at room temperature. Piperidine (50 drops) was added and the reaction was stirred at room temperature for 3 days. A yellow solid was recovered by filtration and washed with toluene to afford 6MNEP-T (65 %yield).

6DMIQ and 6MEIQ derivatives were obtained using Wittig and Heck reactions. The different steps to obtain 6DMIQ-T are detailed below:

***N,N-dimethyl-4-vinylaniline*:** To a stirred solution of methyltriphenylphosphonium bromide in dry THF (1 eq, 0.12 M), *n*-Butyl lithium (1 eq) was added dropwise. The resulting solution was stirred for 15 minutes and then 4-(dimethylamino)benzaldehyde (1 eq) was added. After 3h, saturated ammonium chloride was added and the resulting mixture was extracted with DCM. The extracted organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The final product was purified by column chromatography (1:2, ethyl acetate:hexanes)

***(E)-4-(2-(isoquinolin-6-yl)vinyl)-N,N-dimethylaniline*:** N,N-dimethyl-4-vinylaniline (1.25 eq) was combined with 6-bromoisoquinoline (1 eq) in dry trimethylamine. The $Pd(OAc)_2$ catalyst (0.02 eq) and tri-otolyl phosphine (0.04 eq) were added and the reaction was stirred

for 48h at 80°C. The reaction mixture was concentrated by evaporation of the solvent and column chromatography (1:4, ethyl acetates:hexanes) afforded the purified coupled product.

***(E)-6-(4-(dimethylamino)styryl)-2-methylisoquinolin-2-ium 4-methylbenzenesulfonate (6DMIQ-T)*:** The coupled product obtained in the previous step was reacted with methyl 4-methylbenzenesulfonate in toluene at 80°C for 24h. The resulting organic salt was collected by filtration. (Yield, 98%)

NMR characterization was performed in a 500 MHz spectrometer. All compounds were dissolved in DMSO-d6 and the shifts are reported with respect to TMS.

***(E)-6-(4-methoxystyryl)isoquinoline (6MEIQ)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 9.195 (s, 1H), 8.501 (s, 1H), 7.932 (d, J: 8.01Hz, 1H), 7.826 (d, J: 8.01Hz, 1), 7.784 (s, 1H), 7.612 (s, 1H), 7.520 (d, J: 7.01Hz), 7.296-7.232 (m, 3H), 7.180-7.098 (m, 1H), 6.942 (d, J: 7.01Hz, 2H), 3.853 (s, 3H).

***(E)-4-(2-(6-methoxynaphthalen-2-yl)vinyl)-1-methylpyridin-1-ium 4-methylbenzenesulfonate (6MNEP-T)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.842 (d, J: 6.72 Hz, 2H) 8.221 (d, J: 6.60 Hz, 2H), 8.126 (t, 2H), 7.915 (m, 3H), 7.574 (d, J: 16.38Hz, 1H), 7.465 (d, J: 7.94 Hz, 2H), 7.391 (d, J: 2.32 Hz, 1H), 7.235 (dd, J1: 2.44 Hz, J2: 6.48 Hz, 1H), 7.10 (d, J: 7.95 Hz, 2H), 4.247 (s, 3H), 3.906 (s, 3H), 2.279 (s, 3H). Yield: 42%.

***(E)-4-(2-(6-methoxynaphthalen-2-yl)vinyl)-1-methylpyridin-1-ium 4-nitrobenzenesulfonate (6MNEP-4NBS)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.822 (d, J:6.72 Hz, 2H), 8.205 (m, 4H), 8.105 (t, 2H), 7.917 (m, 3H), 7.8425 (t, 2H), 7.573 (d, J: 16.26 Hz, 1H), 7.441 (d, J: 12.35 Hz, 1H), 7.211 (dd, J1: 2.57 Hz, J2: 6.35 Hz, 1H), 4.247 (s, 3H), 3.906 (s, 3H). Yield: 45%.

***(E)-6-(4-methoxystyryl)-2-methylisoquinolin-2-ium 4-methylbenzenesulfonate (6MEIQ-T)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 9.805 (s, 1H), 8.594 (s, 1H), 8.427-8.374 (m, 2H), 8.375-8.288 (m, 2H), 7.775-7.662 (m, 3H), 7.489-7.296 (m, 3H), 7.106 (d, J: 6.61Hz, 2H), 7.036 (d, J: 6.61Hz, 2H), 4.413 (s, 3H), 3.817 (s, 3H), 2.284 (s, 3H). Yield: 44%.

***(E)-6-(4-methoxystyryl)-2-methylisoquinolin-2-ium 4-nitrobenzenesulfonate (6MEIQ-4NBS)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 9.798 (s, 1H), 8.606 (d, J: 6.88 Hz, 1H), 8.407 (t, J: 6.69 Hz, 2H), 8.356-8.308 (m, 2H), 8.201 (d, J: 6.84 Hz, 2H), 7.832 (d, J: 6.85 Hz, 2H), 7.753-7.696 (m, 3H), 7.452 (d, J: 16.33 Hz, 1H), 7.041 (d, J: 8.78 Hz, 2H), 4.412 (s, 3H), 3.820 (s, 3H). Yield: 47%.

***4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium 4-methylbenzenesulfonate (MBDM-T)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.8567 (d, J:6.73Hz 2H), 7.8758-7.7821 (m, 4H), 7.5121 (m, 3H), 7.1509 (d, J: 7.46Hz, 2H), 7.0109-6.837 (m, 4H), 6.5653 (d, J: 15.74Hz, 1H), 4.468 (s, 3H), 3.8509 (s, 3H), 2.3367 (s, 3H). Yield: 54%.

***4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium 4-nitrobenzenesulfonate (MBDM-4NBS)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.758 (d, J: 6.6 Hz, 2H), 8.193 (d, J: 8.68 Hz, 2H), 8.095 (d, J: 6.73 Hz, 2H), 7.827 (d, J: 8.8 Hz, 2H), 7.604 (d, J: 8.55 Hz, 2H), 7.156-1.104 (m, 2H), 7.057-6.977 (m, 3H), 6.824 (d, J: 15.4 Hz, 2H), 4.105 (s, 3H), 3.792 (s, 3H). Yield: 53%.

***(E)-6-(4-(dimethylamino)styryl)-2-methylisoquinolin-2-ium 4-methylbenzenesulfonate (6DMIQ-T)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 9.725 (s, 1H), 8.546 (d, J: 6.84, 1H), 8.345-8.287 (m, 3H), 8.220 (s, 1H), 7.673 (d, J: 16 Hz, 1H), 7.578 (d, J: 8.8 Hz, 2H), 7.463 (d, J: 7.81 Hz, 2H), 7.288 (d, J: 16 Hz, 1H), 7.103 (d, J: 7.82 Hz, 2H), 6.776 (d, J: 8.68, 2H), 4.380 (s, 3H), 2.992 (s, 6H), 2.281 (s, 3H). Yield: 57%.

***(E)-6-(4-(dimethylamino)styryl)-2-methylisoquinolin-2-ium 4-nitrolbenzenesulfonate (6DMIQ-4NBS)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 9.732 (s, 1H), 8.520 (d, J: 6.84, 1H), 8.315-8.287 (m, 3H), 8.220 (s, 1H), 7.873 (d, J: 16 Hz, 1H), 7.653 (d, J: 8.8 Hz, 2H), 7.385 (d, J: 7.81 Hz, 2H), 7.236 (d, J: 16 Hz, 1H), 7.154 (d, J: 7.82 Hz, 2H), 6.798 (d, J: 8.68, 2H), 4.360 (s, 3H), 2.925 (s, 6H), 2.302 (s, 3H). Yield: 51%.

***4-((1E,3E)-4-(4-(dimethylamino)phenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium 4-methylbenzenesulfonate (DACS-T)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.690 (d, J: 6.88 Hz, 2H), 8.217-8.8.183 (m, 2H), 8.024 (d, J: 6.88Hz, 2H), 7.859-7.763 (m, 3H), 7.471 (d, J: 8.60 Hz, 2H), 7.021-6.996 (m, 2H), 6.752-6.697 (m, 3H), 4.181 (s, 3H), 3.311 (s, 3H), 2.988 (s, 6H). Yield: 49%.

***4-((1E,3E)-4-(4-(dimethylamino)phenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium 4-nitrobenzenesulfonate (DACS-4NBS)*:** ^{1}H NMR (500 MHz, C_2D_6OS), 8.687 (s, 2H), 8.194 (d, J: 6.70Hz, 2H), 8.018 (s, 2H), 7.857-7.750 (m, 3H), 7.469 (d, J: 7.81Hz, 2H), 7.005 (s, 2H), 6.759-6.690 (m, 3H), 4.177 (s, 3H), 2.986 (s, 6H). Yield: 47%.

2. X-ray diffraction analysis

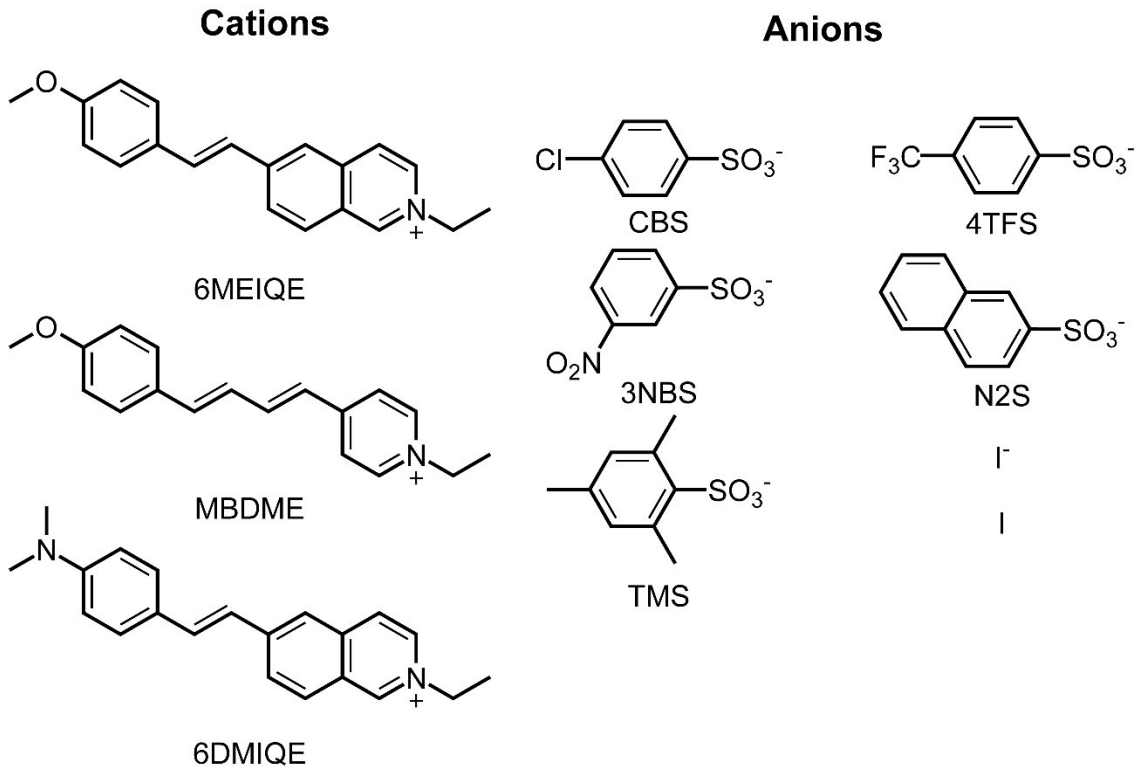

Figure S1 Molecular structures of ethylated cations, sulfonate anions and iodide

6MNEP-T: *Crystal System*, triclinic; *Space Group*, P1; *Point group*, -1; a, 6.9488(3) Å; *b*, 8.1027(4) Å; *c*, 9.9927(5) Å; *a*, 104.045(3)°; *β*, 97.177(3)°; *γ*, 93.047(3)°; *z*, 1; R_1, 0.0353; wR_2, 0.0867; *GOF*, 1.069; *CCDC*: 1867834

6MNEP-T (296 K): *Crystal System*, triclinic; *Space Group*, P1; *Point group*, -1; a, 7.0739(2) Å; *b*, 8.1024(2) Å; *c*, 10.0726 Å; *a*, 103.779(1)°; *β*, 98.209(1)°; *γ*, 91.338(1)°; *z*, 1; R_1, 0.0574; wR_2, 0.1592; *GOF*, 1.074; *CCDC*: 2006490

6MNEP-4NBS: *Crystal System*, triclinic; *Space Group*, P1; *Point group*, -1; a, 7.1520(2) Å; *b*, 7.9596(3) Å; *c*, 9.8172(3) Å; *a*, 102.972(2)°; *β*, 96.957(2)°; *γ*, 91.888(2)°; *z*, 1; R_1, 0.0267; wR_2, 0.0692; *GOF*, 1.064; *CCDC*: 1867835

6MEIQ-T: *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 8.2355(5) Å; *b*, 11.1247(7) Å; *c*, 12.4991(6) Å; *a*, 86.568(4)°; *β*, 75.984(4)°; *γ*, 88.350(4)°; *z*, 2; R_1, 0.0496; wR_2, 0.1192; *GOF*, 1.072; *CCDC*: 1990758.

6MEIQ-4NBS: *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 10.5725(6) Å; *b*, 6.6821(4) Å; *c*, 32.4379(18) Å; *a*, 90°; *β*, 95.284(3); *γ*, 90°; *z*, 4; R_1, 0.0382; wR_2, 0.1029; *GOF*, 1.030; *CCDC*: 1973403

MBDM-T: *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 8.8320(6) Å; *b*, 6.6710(5) Å; *c*, 36.675(3) Å; *a*, 90°; *β*, 95.170(5); *γ*, 90°; *z*, 4; R_1, 0.0418; wR_2, 0.1086; *GOF*, 1.045; *CCDC*: 1962606

MBDM-4NBS: *Crystal System*, orthorhombic; *Space Group*, $P2_12_12_1$; *Point group*, 222; a, 6.6719(3) Å; *b*, 7.9424(4) Å; *c*, 39.7008(19) Å; *a*, 90°; *β*, 90°; *γ*, 90°; *z*, 4; R_1, 0.0435; wR_2, 0.1114; *GOF*, 1.045; *CCDC*: 1961452

6DMIQ-T: *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 10.1028(5) Å; *b*, 10.3242(6) Å; *c*, 13.4088(7) Å; *a*, 101.539(2)°; *β*, 108.960(2)°; *γ*, 106.377(2)°; *z*, 2; R_1, 0.0618; wR_2, 0.1669; *GOF*, 1.041; *CCDC*: 1960837

6DMIQ-4NBS monohydrate 1: *Crystal System*, monoclinic; *Space Group*, C2/c; *Point group*, 2/m; a, 38.437(2) Å; *b*, 7.1832(5) Å; *c*, 20.0502(13) Å; *a*, 90°; *β*, 121.085(3)°; *γ*, 90°; *z*, 8; R_1, 0.0479; wR_2, 0.1381; *GOF*, 1.040; *CCDC*: 1916881

6DMIQ-4NBS monohydrate 2: *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 17.8624(4) Å; *b*, 8.1056(2) Å; *c*, 17.3004(4) Å; *a*, 90°; *β*, 110.784°; *γ*, 90°; *z*, 4; R_1, 0.0484; wR_2, 0.1314; *GOF*, 1.083; *CCDC*: 1916886

DACS-T: *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 9.7592(5) Å; *b*, 10.6361(5) Å; *c*, 13.0359(6) Å; *a*, 109.272(3)°; *β*, 99.244(3)°; *γ*, 108.409(3)°; *z*, 2; R_1, 0.0396; wR_2, 0.1118; *GOF*, 1.040; *CCDC*: 1963594

DACS-4NBS: *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 7.5802(6) Å; *b*, 17.0433(13) Å; *c*, 17.5161(14) Å; *a*, 90°; *β*, 91.416(6); *γ*, 90°; *z*, 4; R_1, 0.0473; wR_2, 0.1212; *GOF*, 1.124; *CCDC*: 1964071

6MNEP-4CF3 (*(E)-4-(2-(6-methoxynaphthalen-2-yl)vinyl)-1-methylpyridin-1-ium 4-(trifluoromethyl)benzenesulfonate)*: *Crystal System*, monoclinic; *Space Group*, Pn; *Point group*, m; a, 7.8208(3) Å; *b*, 7.1973(3) Å; *c*, 19.9675(8) Å; *a*, 90°; *β*, 96.700(2)°; *γ*, 90°; *z*, 2; R_1, 0.0278; wR_2, 0.0727; *GOF*, 1.054; *CCDC*: 1960849

6MNEP-3NBS (*(E)-4-(2-(6-methoxynaphthalen-2-yl)vinyl)-1-methylpyridin-1-ium 4-(trifluoromethyl)benzenesulfonate)* : *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 19.6595(7) Å; *b*, 6.4297(2) Å; *c*, 17.8266(6) Å; *a*, 90°; *β*, 104.903(2)°; *γ*, 90°; *z*, 2; R_1, 0.0383; wR_2, 0.1015; *GOF*, 1.046; *CCDC*: 1960848

6MEIQE-4NBS (*(E)-2-ethyl-6-(4-methoxystyryl)isoquinolin-2-ium 4-nitrobenzenesulfonate)*: *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 7.085(3) Å; *b*, 7.315(2) Å; *c*, 22.030(7) Å; *a*, 90.112(9)°; *β*, 96.227(10)°; *γ*, 92.400(18)°; *z*, 2; R_1, 0.0338; wR_2, 0.0859; *GOF*, 1.032; *CCDC*: 1973431

MBDM-N2S (*4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-1-methylpyridin-1-ium naphthalene-2-sulfonate)*: *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 9.6916(4) Å; *b*, 10.6359(5) Å; *c*, 11.1871(5) Å; *a*, 78.992(2)°; *β*, 79.976(2)°; *γ*, 89.669(2)°; *z*, 2; R_1, 0.0317; wR_2, 0.0828; *GOF*, 1.049; *CCDC*: 1960838

MBDME-3NBS (*1-ethyl-4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)pyridin-1-ium 3-nitrobenzenesulfonate)* : *Crystal System*, monoclinic; *Space Group*, $P2_1/c$; *Point group*, 2/m; a, 6.3747(2) Å; *b*, 38.0176(14) Å; *c*, 8.8064(3) Å; *a*, 90°; *β*, 92.289(2)°; *γ*, 90°; *z*, 4; R_1, 0.0365; wR_2, 0.0912; *GOF*, 1.063; *CCDC*: 1960839

MBDME-4NBS (*1-ethyl-4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)pyridin-1-ium 4-nitrobenzenesulfonate)*: *Crystal System*, orthorhombic; *Space Group*, $P2_12_12_1$; *Point group*, 222; a, 6.7363(3) Å; *b*, 8.1126(4) Å; *c*, 39.4951(19) Å; *a*, 90°; *β*, 90°; *γ*, 90°; *z*, 4; R_1, 0.0267; wR_2, 0.0685; *GOF*, 1.062; *CCDC*: 1960840

MBDME-CBS (*1-ethyl-4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)pyridin-1-ium 4-chlorobenzenesulfonate)*: *Crystal System*, orthorhombic; *Space Group*, $P2_12_12_1$; *Point group*, 222; a, 6.8059(2) Å; *b*, 7.9943(3) Å; *c*, 39.4102(13) Å; *a*, 90°; *β*, 90°; *γ*, 90°; *z*, 4; R_1,

0.0280; wR_2, 0.0726; *GOF*, 1.035; *CCDC*: 1960847

MBDME-N2S (***1-ethyl-4-((1E,3E)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)pyridin-1-ium naphthalene-2-sulfonate)*:** *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 9.7501(6) Å; *b*, 10.9056(6) Å; *c*, 11.4648(6) Å; *a*, 77.261(3)°; *β*, 79.382(4)°; *γ*, 81.917(3)°; *z*, 2; R_1, 0.0311; wR_2, 0.0834; *GOF*, 1.021; *CCDC*: 1960841

6DMIQE-4NBS ***((E)-6-(4-(dimethylamino)styryl)-2-ethylisoquinolin-2-ium 4-nitrobenzenesulfonate)*** **:** *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 7.5893(7) Å; *b*, 13.5028(11) Å; *c*, 23.829(2) Å; *a*, 95.198(5)°; *β*, 92.280(6)°; *γ*, 99.555(7)°; *z*, 4; R_1, 0.0410; wR_2, 0.1105; *GOF*, 1.064; *CCDC*: 1916880

6DMIQE-3NBS ***((E)-6-(4-(dimethylamino)styryl)-2-ethylisoquinolin-2-ium 3-nitrobenzenesulfonate)*:** *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 8.2165(3) Å; *b*, 9.5708(5) Å; *c*, 15.9375(7) Å; *a*, 97.645(4)°; *β*, 92.675(4)°; *γ*, 93.859(3)°; *z*, 2; R_1, 0.0542; wR_2, 0.1395; *GOF*, 1.047; *CCDC*: 1916882

6DMIQE-CBS ***((E)-6-(4-(dimethylamino)styryl)-2-ethylisoquinolin-2-ium 4-chlorobenzenesulfonate)*:** *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 8.0643(5) Å; *b*, 10.0456(6) Å; *c*, 14.7344(9) Å; *a*, 95.018(3)°; *β*, 96.726(3)°; *γ*, 92.402(3)°; *z*, 2; R_1, 0.0357; wR_2, 0.0916; *GOF*, 1.049; *CCDC*: 1916884

6DMIQE-TMS ***((E)-6-(4-(dimethylamino)styryl)-2-ethylisoquinolin-2-ium 2,4,6-trimethylbenzenesulfonate)*:** *Crystal System*, triclinic; *Space Group*, P-1; *Point group*, -1; a, 8.6019(5) Å; *b*, 10.1226(6) Å; *c*, 15.5819(8) Å; *a*, 95.347(4)°; *β*, 104.070(4)°; *γ*, 105.448(4)°; *z*, 2; R_1, 0.0469; wR_2, 0.1172; *GOF*, 1.030; *CCDC*: 1916885

6DMIQE-I ***((E)-6-(4-(dimethylamino)styryl)-2-ethylisoquinolin-2-ium iodide)*:** *Crystal System*, orthorhombic; *Space Group*, Pbca; *Point group*, mm2; a, 12.7754(6) Å; *b*, 8.5188(5) Å; *c*, 35.3048(16) Å; *a*, 90°; *β*, 90°; *γ*, 90°; *z*, 8; R_1, 0.0422; wR_2, 0.1041; *GOF*, 1.047; *CCDC*: 1916883

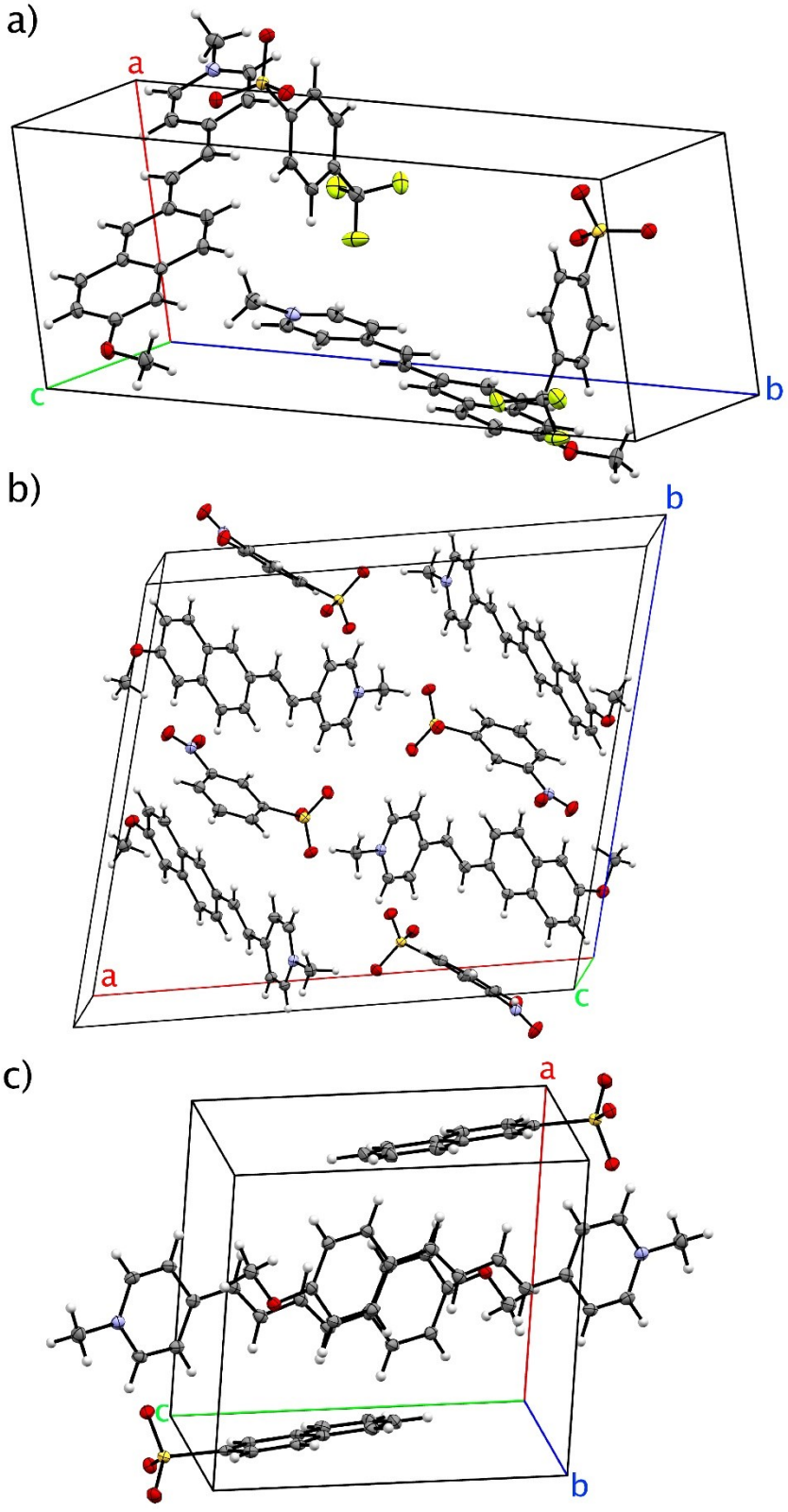

Figure S2 6MNEP and MBDM cations paired with different anions, a) 6MNEP-4TFS, b) 6MNEP-3NBS, and c) MBDM-N2S,

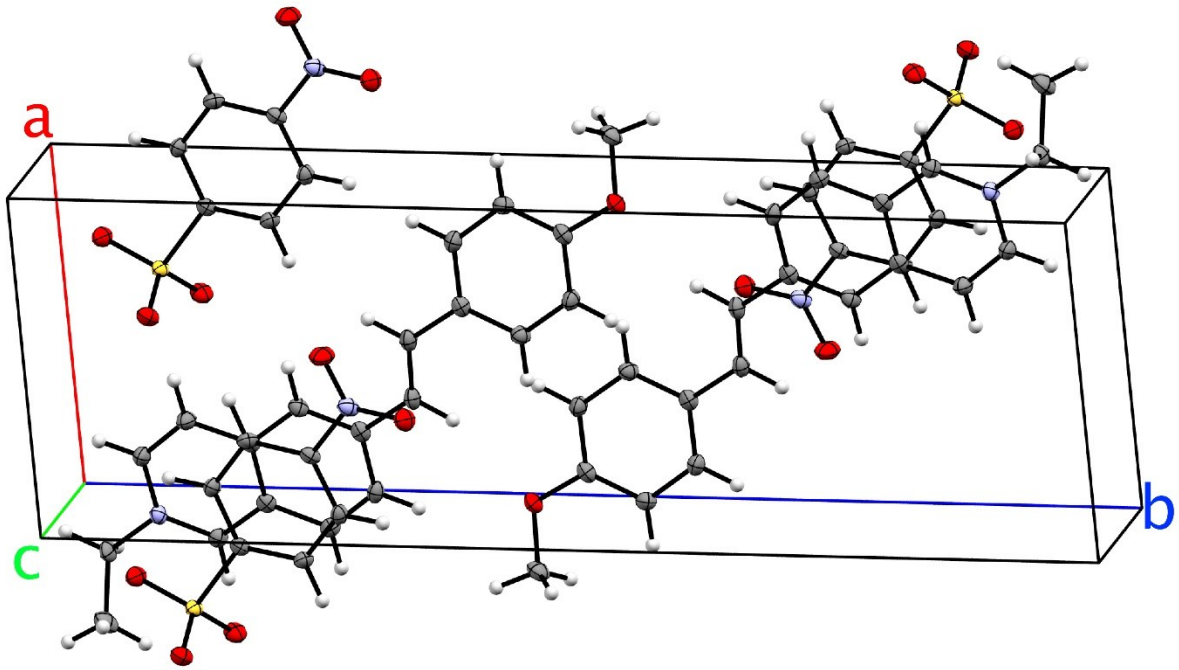

Figure S3 6MEIQE cation paired with different anions, a) 6MEIQE-4NBS

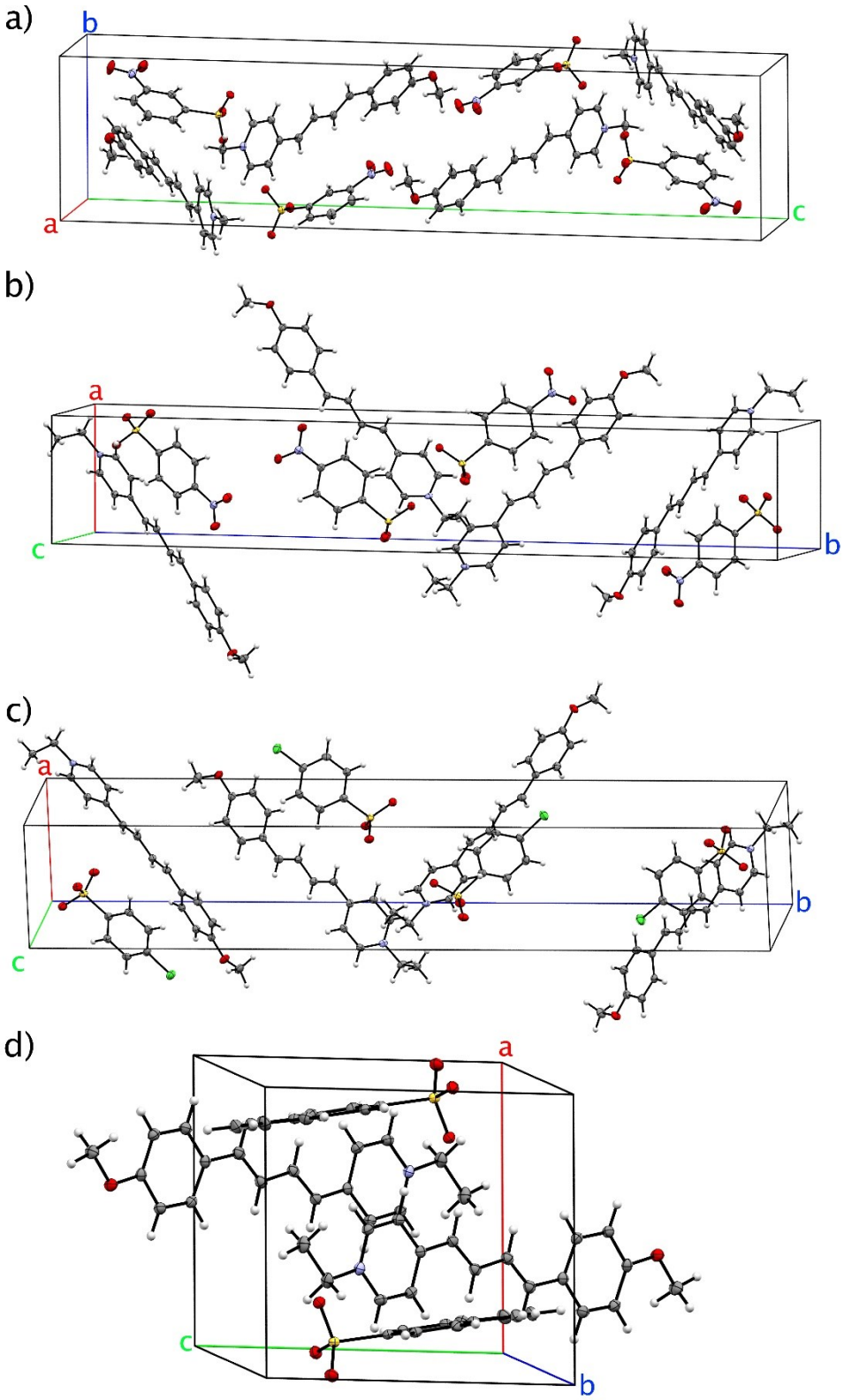

Figure S4 MBDME cation paired with different anions, a) MBDME-3NBS, b) MBDME-4NBS, c) MBDME-CBS, and d) MBDME-N2S

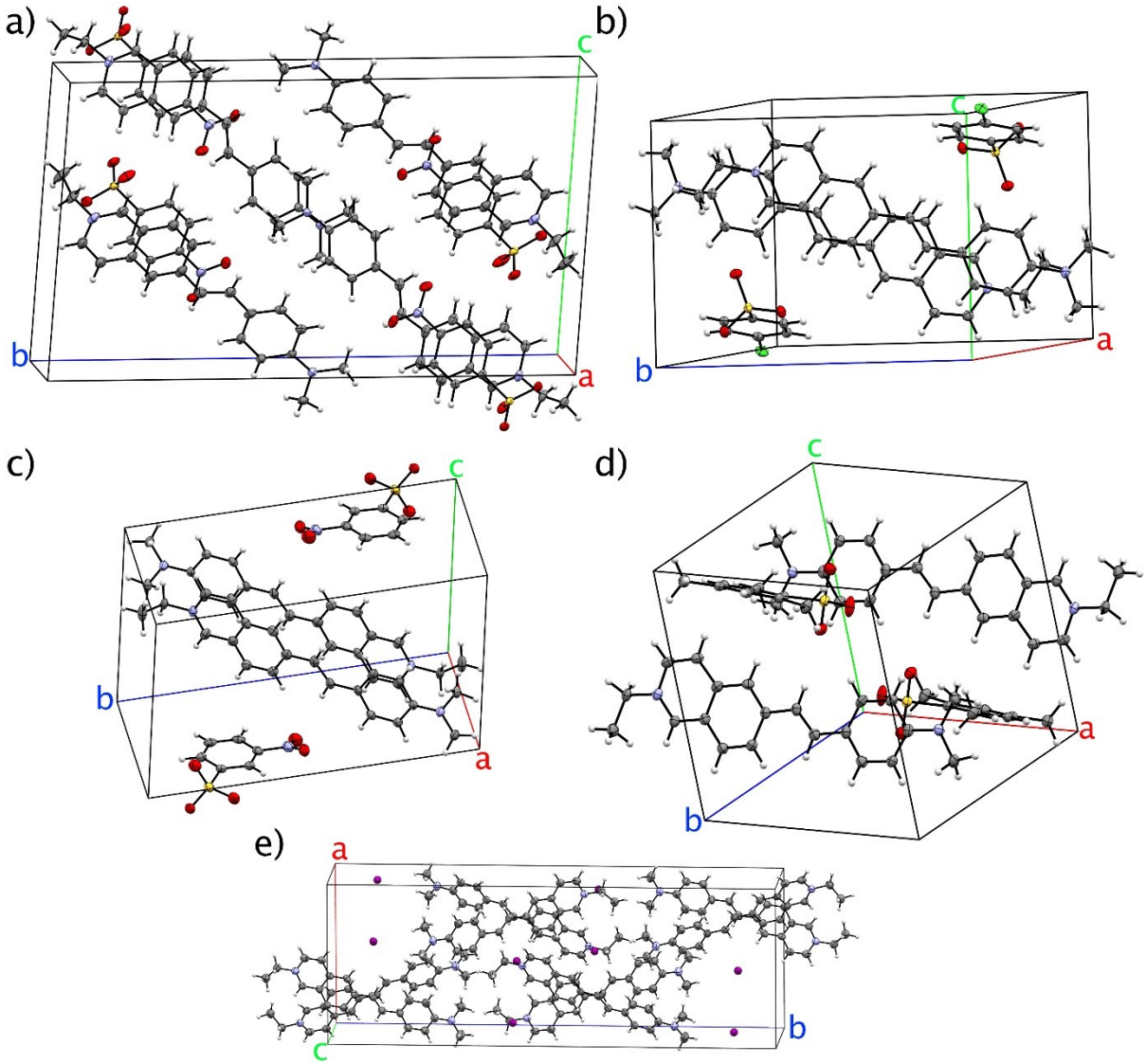

Figure S5 6DMIQE cation paired with different anions, a) 6DMIQE-4NBS, b) 6DMIQE-CBS, c) 6DMIQE-3NBS, d) 6DMIQE-TMS, and e) 6DMIQE-I.

3. Light absorption and transmission data

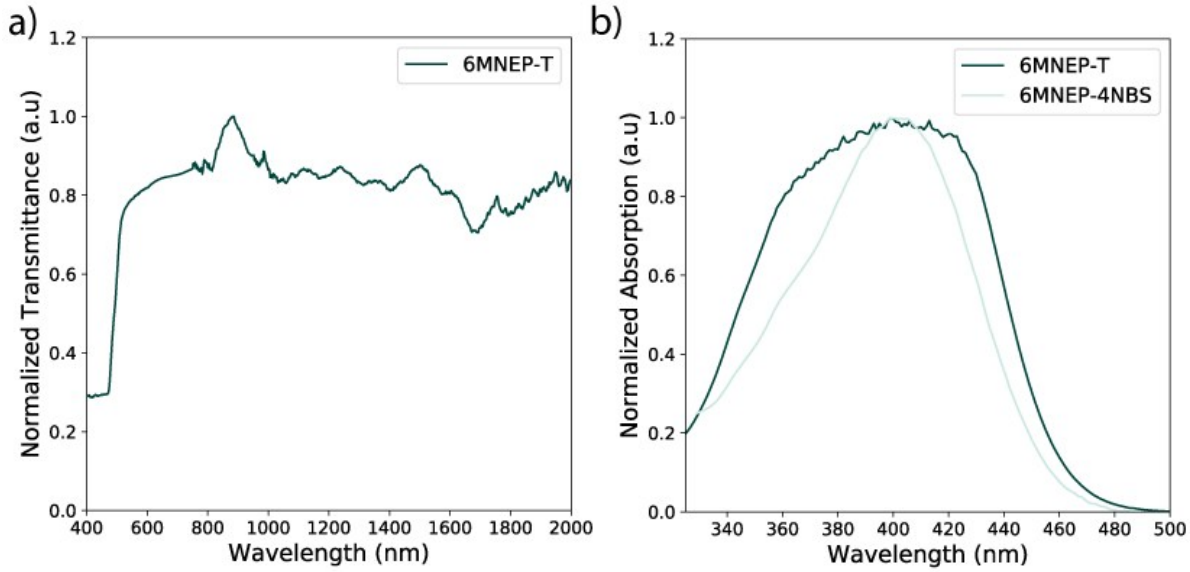

Figure S6 a) Transmittance spectrum for a 6MNEP-T crystalline sample, and b) Methanol solution absorption measurements for 6MNEP-T and 6MNEP-4NBS.

4. Quantum calculations optimization

To establish a thorough comparison between the featured 6MNEP chromophores and other NLO organic crystals, we performed β calculations, with different DFT functionals, as detailed in **Table S1**. 6MNEP compounds showed better performance compared with DAST, HMQ-TMS, HMQ-T, and OHP-CBS with all of the tested DFT functionals. In addition, we show the data for B3LYP/NLO-V and cam-B3LYP/NLO-V calculations due to the recently shown efficiency of using this basis set to obtain fast and reliable results. The same trends as obtained with B3LYP/6-31++g** were found for NLO-V calculations; therefore, we decided to use this basis set for more expensive computations. The hybrid functional B3LYP was selected because of its reliable performance for DFT calculations due to its ability to recover dynamic electron correlation. This is critical for the estimation of hyperpolarizability values that has been shown to be almost exclusively electronic in nature for NLO applications. We decided to test long range corrected CAM-B3LYP due to the larger volume of π-extended molecules featured in this study compared with other state-of-the-art NLO chromophores

Table S1 Hyperpolarizability values (β_{tot}) obtained at different levels of theory. B3LYP, cam-B3LYP, B3P86, and O3LYP functionals were paired with the 6-311++G**. B3LYP and cam-B3LYP were also tested with the NLO-V basis set (marked with *). Values are reported in 10^{-30} esu.

Chromophore/ Functional	DAST	HMQ-TMS	HMQ-T	OHP-CBS	6MNEP-T	6MNEP-4NBS
B3LYP	200	186	171	115	305	301
B3LYP*	188	209	183	115	318	311
cam-B3LYP	231	131	138	110	252	257
cam-B3LYP*	216	158	158	119	286	290
B3P86	197	186	171	114	301	297
O3LYP	185	207	183	158	312	306

*NLO-V

5. Molecular arrangements for two and four parts calculations

Figure S7 shows the molecular conformations employed in four cation calculations. The top layer of two cations was removed to perform two cation calculations.

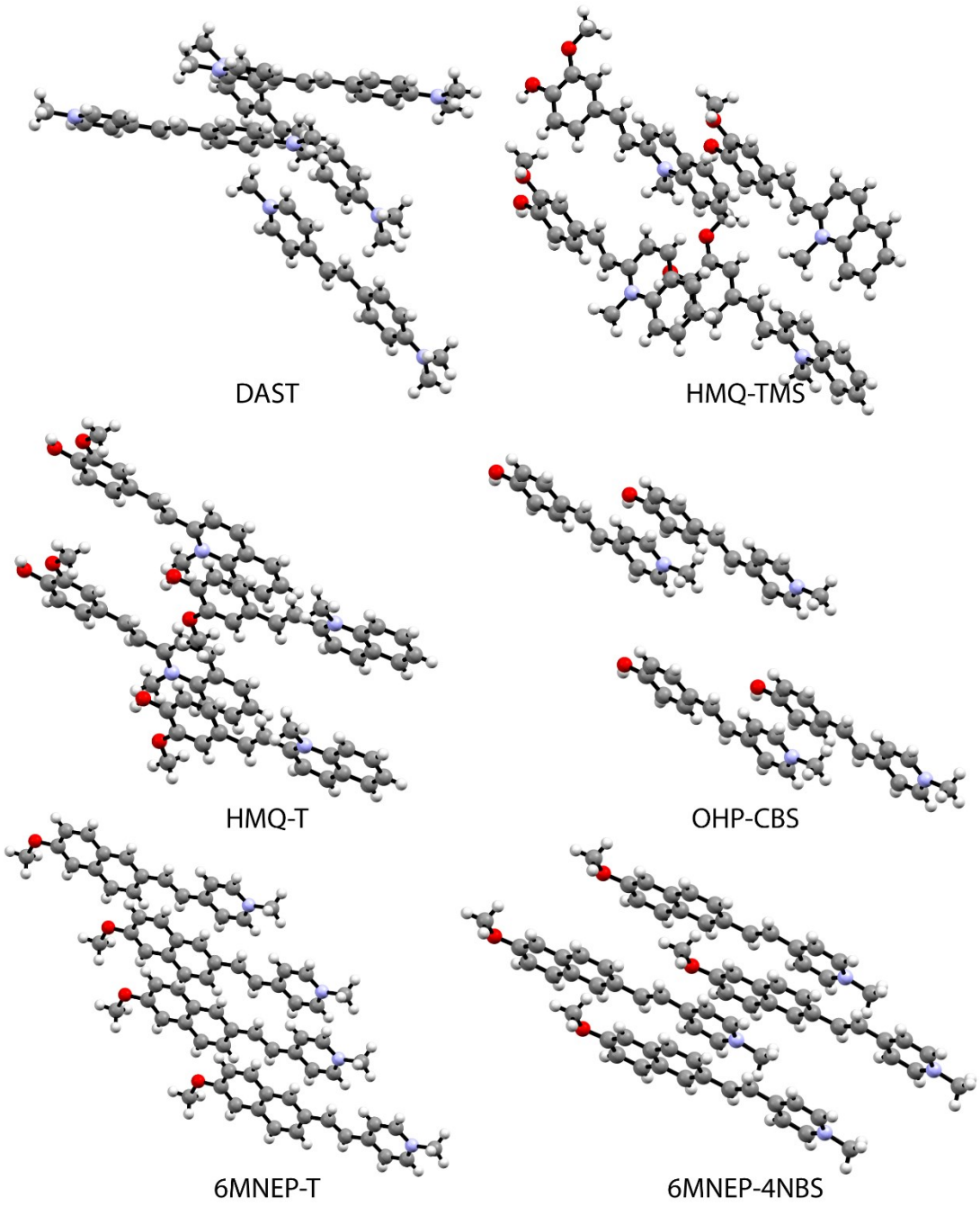

Figure S7 Molecular conformations obtained from crystal structures and utilized to perform four parts calculations.

6. Differential Scanning Calorimetry Data

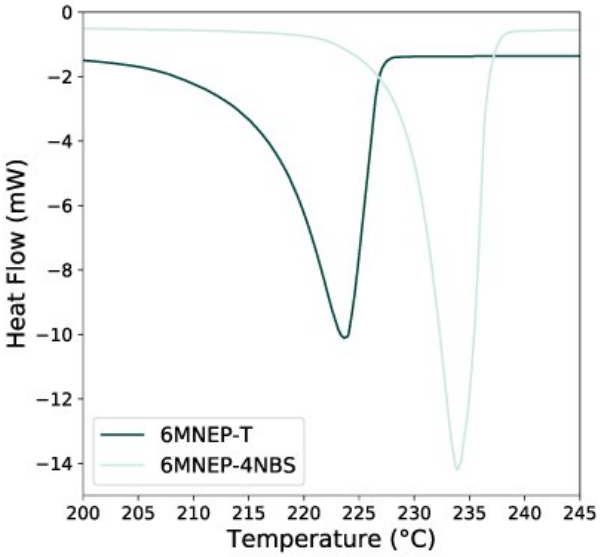

Figure S8 Intermolecular distances for 6MNEP-T and 6MNEP-4NBS compounds.