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Supporting Information

Rational Design and Synthesis of Polythioureas as Capacitor Dielectrics

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Synthesis and Chemical Structure Determination

PDTA-ODA: To a dry 50ml 3-neck flask, 0.961g (5mmol) of para-phenylene diisothiocyanate 1.001g (5mmol) 4,4'-oxydianiline and 20ml NMP were added under inert atmosphere with stirring. After 6h at room temperature, the reaction mixture was poured into methanol with fibre-like precipitation, followed by washing with methanol and dried at 50°C *in vacuo* overnight. White precipitate was obtained in 91% yield (1.78g). FTIR: ν_{max}/cm^{-1} 3210 (N-H st), 3030 (ar C-H st), 1510 (ar C-C), 1340 (C-N st), 1240 (C=S st), 1160 and 1010 (ar C-O-C st). ^{1}H NMR δ_H(500 MHz; DMSO-d^6) 6.99 (4 H, d, benzene), 7.43 (4 H, s, benzene), 7.46 (4 H, d, benzene) and 9.72 (4 H, s, NH). Chain end: 4.98 (0.0736 H, s, NH_2), M_n=21537 g/mol.

PDTC-MDA: The preparation is similar to that of PDTC-ODA, with 0.961g (5mmol) of para-phenylene diisothiocyanate and 0.991g (5mmol) of 4,4'-diphenylmethanediamine. White fibre-like solid was obtained in 94 % yield (1.84g). FTIR: ν_{max}/cm^{-1} 3220 (N-H st), 3020 (ar C-H st), 1510 (ar C-C), 1300 (C-N st), 1250 (C=S st). ^{1}H NMR δ_H(500 MHz; DMSO-d^6) 3.88 (2 H, s, CH_2), 7.20 (4 H, d, benzene), 7.37 (4 H, s, benzene), 7.41 (4 H, d, benzene) and 9.71 (4 H, s, NH). Chain end: 5.24 (0.0280 H, s, NH_2), M_n=56360 g/mol.

PDTC-PhDA: The preparation is similar to that of PDTC-ODA, with 0.961g (5mmol) of para-phenylene diisothiocyanate and 0.991g (5mmol) of 4,4'-diphenylmethanediamine. White fibre-like solid was obtained in 94 % yield (1.84g). FTIR: ν_{max}/cm^{-1} 3220 (N-H st), 3020 (ar C-H st), 1510 (ar C-C), 1310 (C-N st), 1250 (C=S st).

PDTC-HDA: The preparation is similar to that of PDTC-ODA, with 0.961g (5mmol) of para-phenylene diisothiocyanate and 0.581g (5mmol) of 1,6-diaminohexane. White fibre-like solid was obtained in 93 % yield (1.43g). FTIR: ν_{max}/cm^{-1} 3220 (N-H st), 3020 (ar C-H st), 2930 (C-H st), 1510 (ar C-C), 1310 (C-N st), 1230 (C=S st). ^{1}H NMR δ_H(500 MHz; DMSO-d^6) 1.32 (4 H, m, CH_2), 1.54 (4 H, m, CH_2), 3.45 (4 H, m, CH_2), 7.33 (4 H, s, benzene), 7.65 (2 H, s, NH), and 9.39 (2 H, s, NH). Chain end: 1.96 (0.0150 H, s, NH_2), M_n = 85121 g/mol.

PDTC-HK511: The preparation is similar to that of PDTC-ODA, with 0.961g (5mmol) of para-phenylene diisothiocyanate and 1.10g (5mmol) of Jeffamine HK511. White fibre-like solid was obtained in 87 % yield (1.80g). FTIR: ν_{max}/cm^{-1} 3230 (N-H st), 3040 (ar C-H st), 2973 (C-H st), 1510 (ar C-C), 1310 (C-N st), 1230 (C=S st), 1103 and 1038 (ar C-O-C st). ^{1}H NMR δ_H(500 MHz; DMSO-d^6) 1.06-1.13 (7 H, m, Me), 3.52-3.56 (12 H, m, CH_2), 4.49 (2 H, m, CH), 7.36 (4 H, s, benzene), 7.52 (2 H, s, NH), and 9.44 (2 H, s, NH). Chain end: 1.27 (0.0641 H, s, NH_2), M_n = 25975 g/mol.

Thiophosgene-MDA: To a completely dried four neck flask equipped with dropping funnel, distillation and a safety trap, 3.96g 4,4'-diphenylmethanediamine and 2.26g 1,4-diazabicyclo [2.2.2]octane (DABCO) were well mixed then cooled with ice bath. 2.30g thiophosgene was

carefully and slowly added to the mixture through dropping funnel at 0^{o}C. The reaction was then carried out at room temperature for 24h. Deionized water and methanol was used for precipitation and washing, followed by drying 50^{o}C *in vacuo*. Light yellow fibre like polymer was obtained after purification in 85% yield (4.10g). FTIR: ν_{max}/cm^{-1} 3210 (N-H st), 3020 (ar C-H st), 1510 (ar C-C), 1320 (C-N st), 1250 (C=S st). ^{1}H NMR δ_{H}(500 MHz; DMSO-d^{6}) 3.86 (2 H, s, CH_2), 7.18 (4 H, d, benzene), 7.35 (4 H, d, NH), and 9.67 (2 H, s, NH). Chain end: 6.93 (0.0931 H, m, two benzene), M_n=44615 g/mol.

Thin Film Processing

PDTC-ODA: A 10wt% DMSO solution was used for casting large scale film on a borosilicate glass substrate by Dr. Blade Film Applicator. The blade gap was 254µm. Films were casted at 80 ^{o}C followed by drying on the hot plate at 100 ^{o}C for 6h. After peeling off the glass, films were dried under vacuum at 120 ^{o}C overnight. The film thickness is 13-14µm.

PDTC-MDA: A 10wt% DMAc solution was used for casting large scale film on a borosilicate glass substrate by Dr. Blade Film Applicator. The blade gap was 254µm. Films were casted at 60 ^{o}C followed by drying on the hot plate at 80 ^{o}C for 6h. After peeling off the glass, films were dried under vacuum at 100 ^{o}C overnight. The film thickness is 13-14µm.

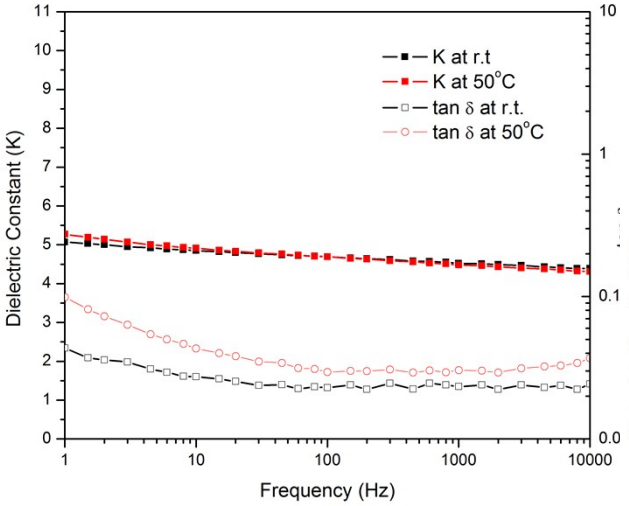
PDTC-HDA: A 10wt% DMAc solution was used for casting large scale film on a borosilicate glass substrate by Dr. Blade Film Applicator. The blade gap was 500µm. Films were casted at 60 ^{o}C followed by drying on the hot plate at 80 ^{o}C for 6h. After peeling off the glass, films were dried under vacuum at 100 ^{o}C overnight. The film thickness is 9-10µm.

PDTC-HK511: A 15wt% DMAc solution was used for casting large scale film on a borosilicate glass substrate by Dr. Blade Film Applicator. The blade gap was 500µm. Films were casted at 70 ^{o}C followed by drying on the hot plate at 75 ^{o}C for 6h. After peeling off the glass, films were dried under vacuum at 100 ^{o}C overnight. The film thickness is 12-14µm.

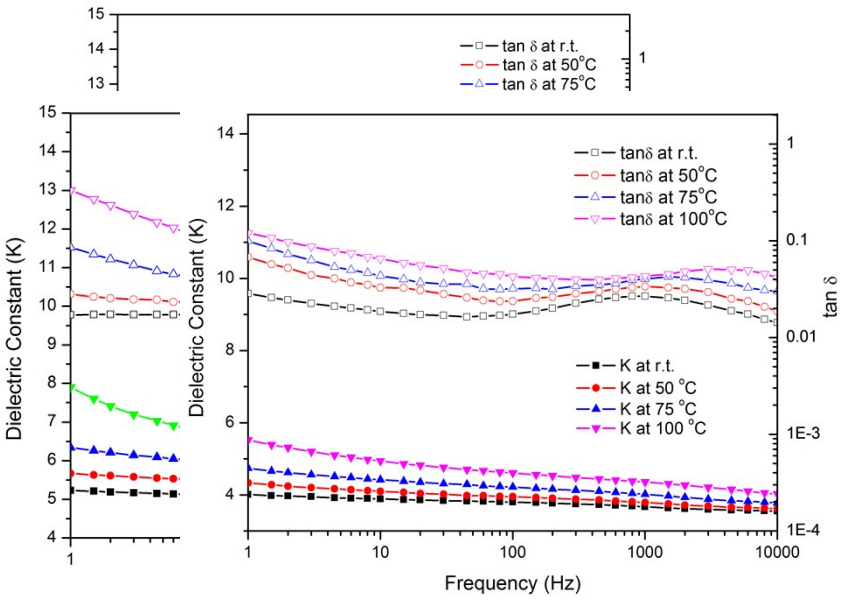
Thiophosgene-MDA: A 15wt% DMSO solution was used for casting large scale film on a borosilicate glass substrate by Dr. Blade Film Applicator. The blade gap was 254µm. Films were casted at 80 ^{o}C followed by drying on the hot plate at 100 ^{o}C for 6h. After peeling off the glass, films were dried under vacuum at 100 ^{o}C overnight. The film thickness is 11-13µm.

Time Domain Dielectric Spectroscopy

PDTC-ODA:



PDTC-MDA:

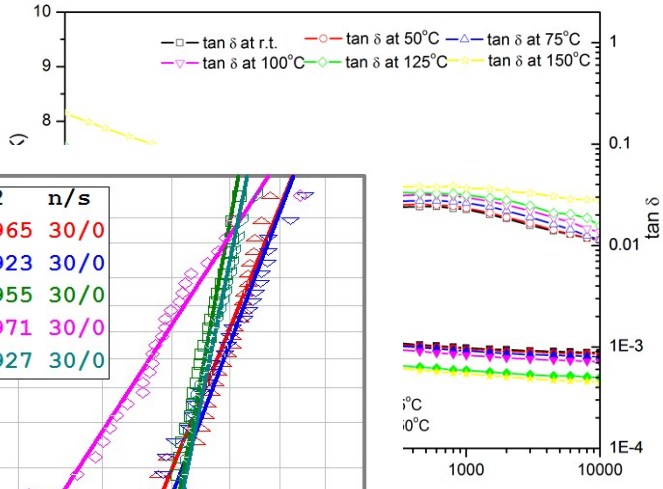


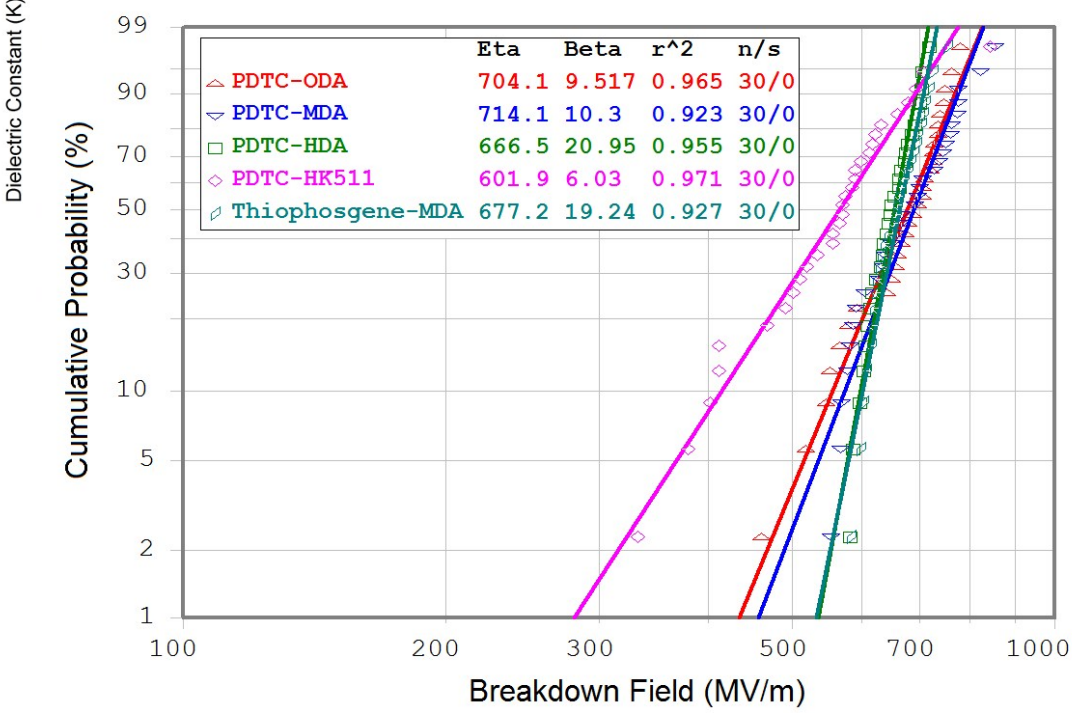
PDTC-PhDA:

PDTC-HDA:

PDTC-HK511:

Thiophosgene-MDA:

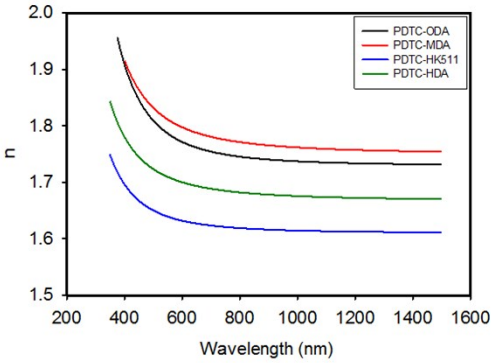


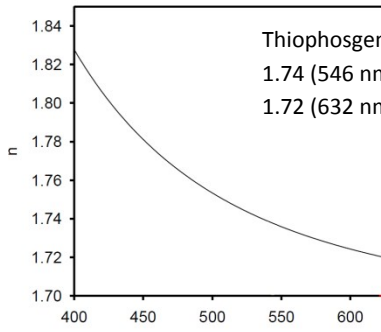


DC Breakdown Field Weibull Distribution

Refractive Index Measurement

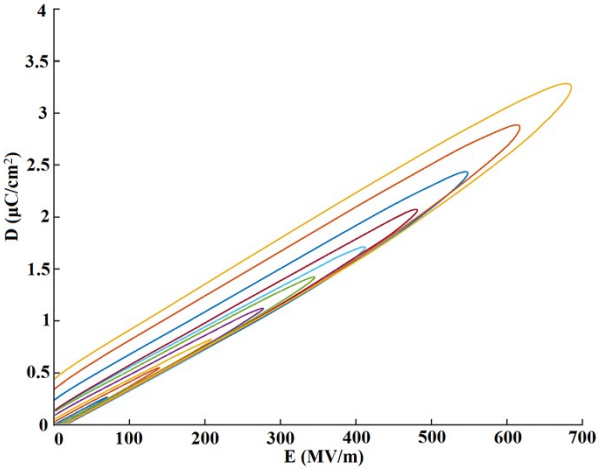
	546 (Green light)	632 (Red light)
PDTC-ODA	1.79	1.76
PDTC-MDA	1.81	1.79
PDTC-HK511	1.64	1.63
PDTC-HDA	1.71	1.70

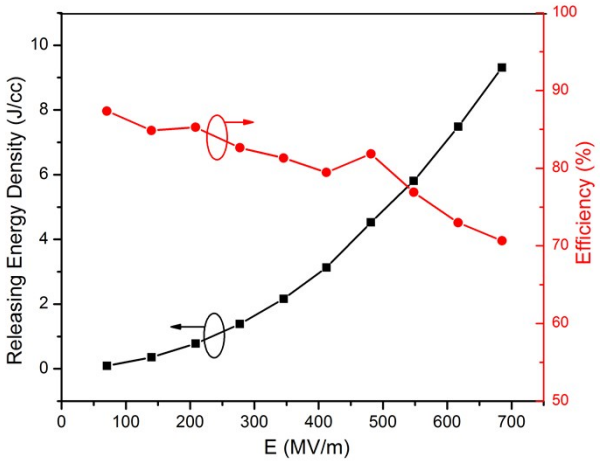




D-E Hysteresis Loop:

PDTC-HDA:





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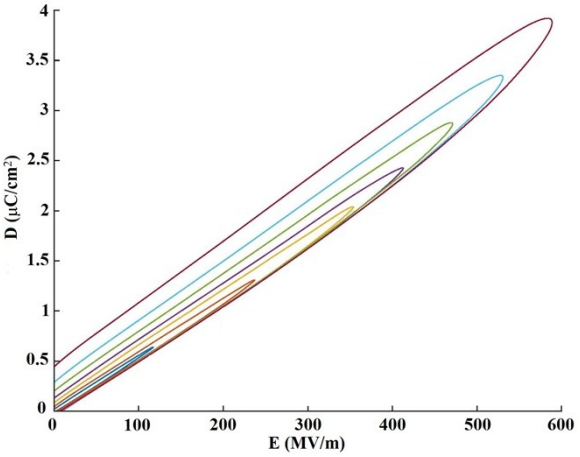

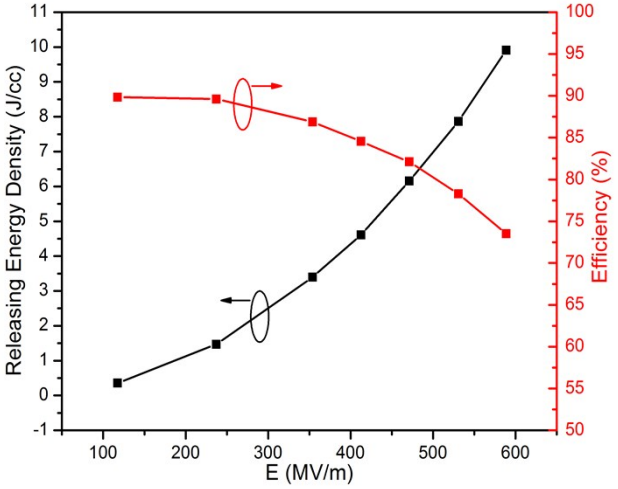

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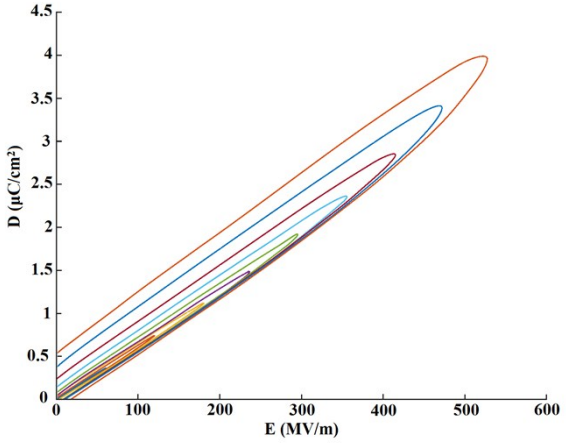
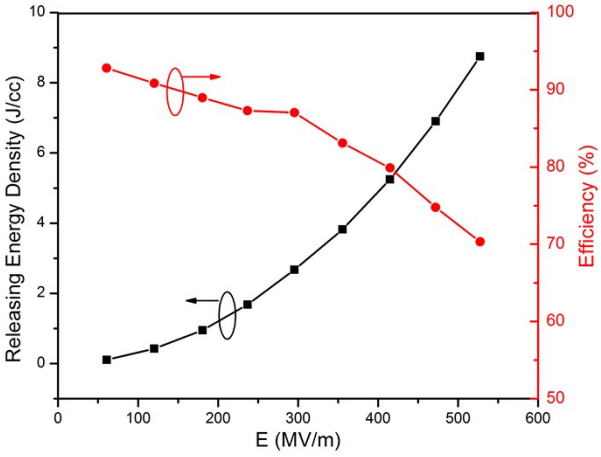
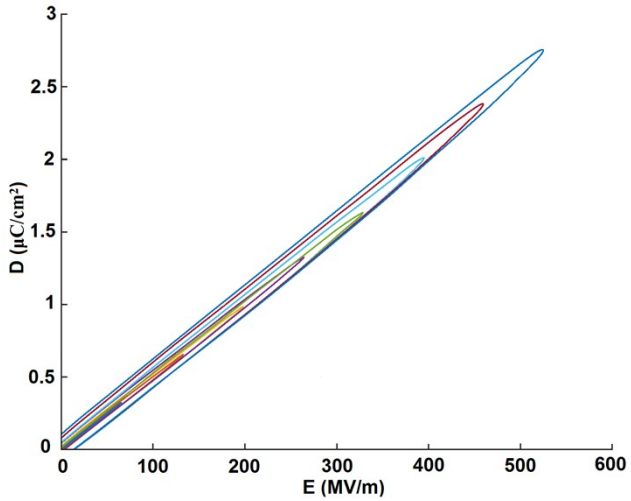
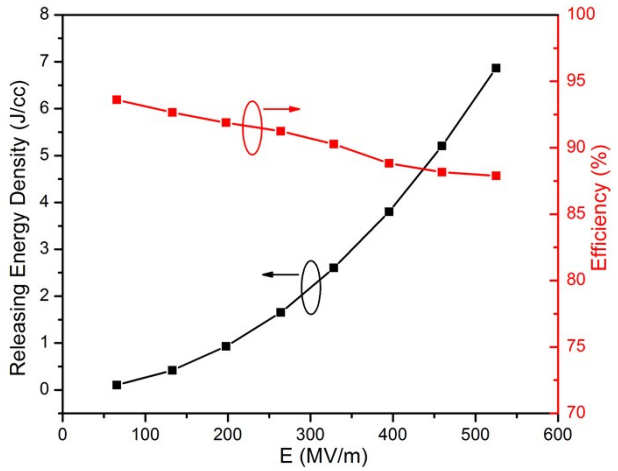




PDTC-HK511:





Thiophosgene-MDA: