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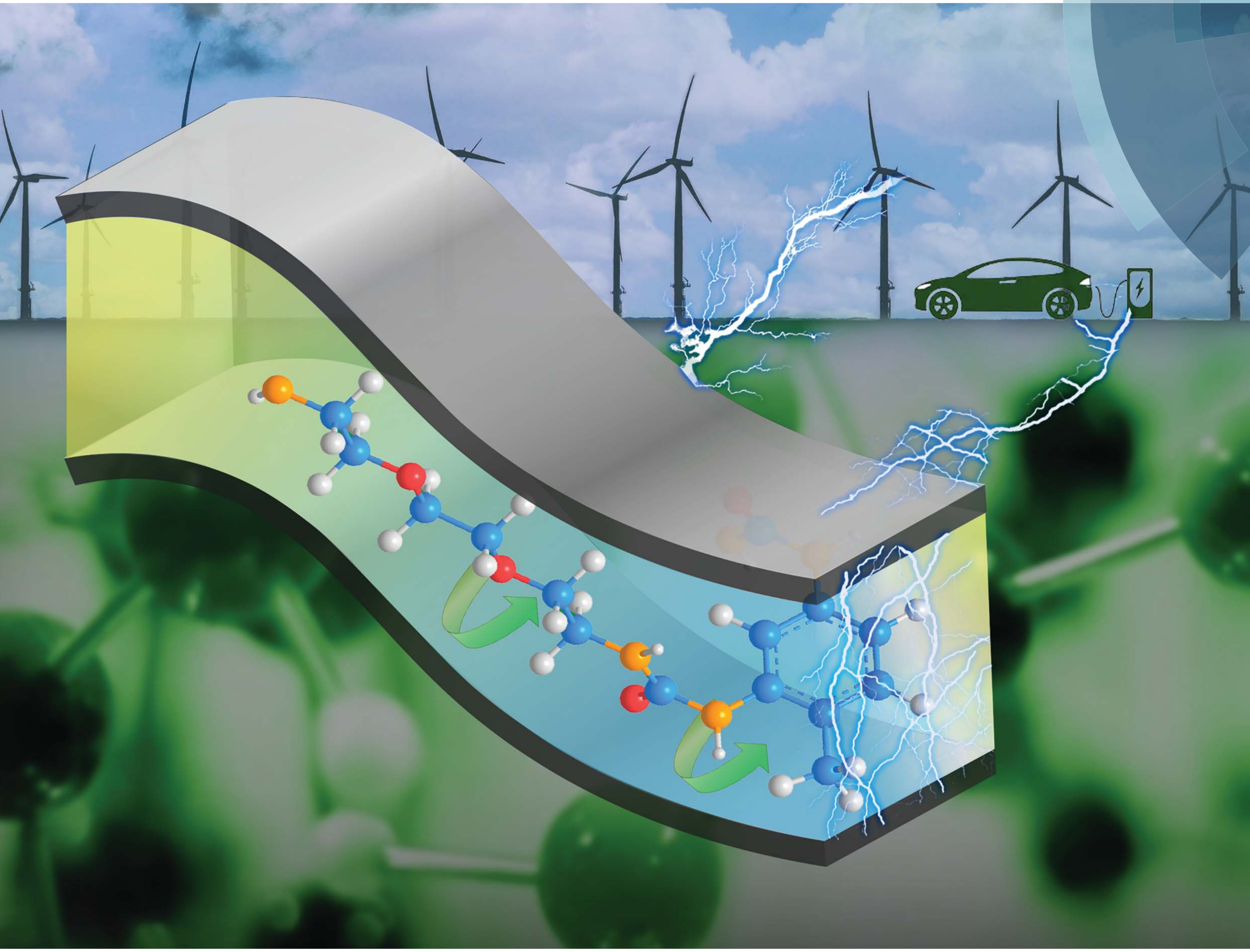

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High energy density and high efficiency all-organic polymers with enhanced dipolar polarization†

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Advanced polymers with high energy density and high efficiency are urgently needed in pulse power capacitor applications. Here, we present a practical design approach towards all-organic polymers with high energy density and high efficiency by enhancing dipolar polarization at the molecular level. Flexible segments were introduced into the backbones of rigid polar aromatic polymers to increase the flexibility of dipoles. Dielectric spectroscopy measurements of designed polymers revealed multiple strong sub-glass transition (sub-T_g) relaxation peaks with low activation energies, which indicated the enhanced movement freedom of dipoles below the glass transition temperature. As a result, dielectric constants were increased up to 46% when compared with their base polymers and *D*–*E* loop measurements showed that all these designed polymers had high energy densities above 11 J cm^{-3} with efficiencies above 90%. These results unveiled a novel approach towards high dielectric constant organic polymers for electrical energy storage.

Polymer film capacitors are widely used as electrical energy storage devices for pulse power supply and power conditioning applications.[1–4] Polymer capacitors have advantages of high voltage scalability, low loss, fast discharge speed and graceful failure mode when compared with ceramic capacitors, supercapacitors or pseudocapacitors.[5] Biaxially oriented polypropylene (BOPP), predominant in commercial polymer film capacitors, has a high breakdown strength (>730 MV m^{-1}) with very high efficiency (>94%). However, its low dielectric constant ($k = 2.2$) results in a limited energy density (~5 J cm^{-3}).[6] Further development in advanced electrical devices to meet future needs calls for new polymers with high energy density as well as high efficiency to replace BOPP.[7]

From the energy density (U) equation $U = 0.5\varepsilon_0\varepsilon_r E^2$ for linear dielectrics, we can see that the energy density can be enhanced by increasing the dielectric constant (ε_r) or breakdown strength (E). Currently, the highest breakdown strength for all-organic polymers is ~1 GV m^{-1}, with limited room for further improvement. Therefore, increasing the dielectric constant appears to be a more practical approach. Intensive research has been carried out towards miniaturized polymer film capacitors with high *k* polymers.[8] A straightforward solution was to introduce high dielectric constant inorganic fillers into the polymer matrix by materials engineering. Materials including polymer blends,[9] nanolaminates,[10] nanocomposites,[11,12] nanocoatings,[13] *etc.* have been demonstrated with high dielectric constants. However, until now, no such polymers have been used in capacitors due to fundamental limitations. Inorganic fillers could lead to low efficiency because of mismatch between the filler and polymer matrix. The existence of the interface was a potential threat for long-term reliability and made large-scale film fabrication challenging.[14]

Thus, it is highly imperative to synthesize polymers with high dielectric constants and low loss over a broad range of frequencies and temperatures.[15] There are mainly four types of polarization that can contribute to the dielectric constant: electronic, ionic, dipolar (orientational), and interfacial polarization.[16] Interfacial polarization is not desired for capacitor applications because it comes with huge dielectric loss.[17] Electronic and ionic polarization occur at very high frequencies (>10^{11} Hz) with almost no loss penalty and are therefore preferred sources of polarization for energy storage purposes. Rational co-designs of high energy density polymers by utilizing electronic and ionic polarization have identified several polar aromatic and organometallic polymers with high dielectric constants.[18] However, that study also indicated an inverse relationship between the band gap and electronic polarization. In order to maintain a high enough band gap (>4 eV) to support

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the breakdown strength (and hence limited electronic polarization), new all-organic polymers with further enhanced ionic and/or dipolar polarization appear to be the most promising way to increase the dielectric constant beyond 4.[19]

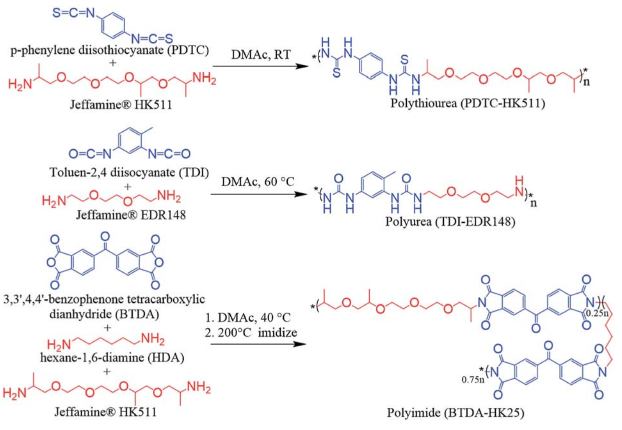
Dipolar polarization, also known as orientational polarization, is an important mechanism that occurs in the frequency range of $\sim 10^8$ Hz with a low dielectric loss. Increasing dipolar polarization can be achieved by utilizing relaxor ferroelectric based copolymers,[20] by introducing polar side groups into glassy polymers,[21,22] or by modifying polymers known for high dielectric constants.[23] It is noteworthy that increasing dipolar polarization in organic polymers often leads to dramatic decreases in discharge efficiency due to multiple loss mechanisms. For example, ferroelectrics suffer from low efficiency because of intrinsic hysteresis loss. By and large, the aforementioned approaches encountered high loss due to strong convoluted coupling between the dipolar orientations and global chain motions. Polymers with a discharge efficiency lower than 90% are generally not practical for capacitor applications because of potential thermal breakdown, regardless of high energy density or high dielectric constants. The main challenge here is to increase dipolar polarization while maintaining the low dielectric loss and other properties.

In this paper, we present a novel yet practical approach to design promising pure organic high *k*, low loss polymers by introducing flexible segments into the backbones of polar aromatic polymers. Specifically, we showed that by introducing flexible ether-linkage segments into the backbones of aromatic polyurea, polythiourea and polyimide, energy densities in these polymers were significantly improved as a result of enhanced dipolar polarization. The enhancement of dipolar polarization was realized *via* "secondary" processes *c.a.* pendant side groups or crank-shaft chain segments undergoing local, uncorrelated re-orientations.[24,25] Furthermore, the aromatic rigid segments ensured sufficiently high glass transitions that decoupled these local re-orientations from primary chain relaxation. These rigid segments also "carved" out free volume to allow increased local re-orientational freedom of dipoles with reduced dipole constraints and thus supported a high discharge efficiency. Three designed polymers were synthesized by addition reactions and free-standing films were produced. A systematic comparative characterization of these novel polymers was given to study their polarization behavior and energy storage capability. Dielectric constants of 4.5–6.6 and loss factors below 0.02 were found in these polymers at room temperature. The dielectric constant showed an increase of >1.5 compared to that of the base polar aromatic polymers. Broadband dielectric spectroscopy revealed strong sub-T_g relaxation peaks, which were related to multiple polarization processes of polar segments. The low activation energy for each relaxation process confirmed the ease of movement of dipoles. *D–E* loop measurements showed that these polymers achieved high energy density (>11 J cm^{-3}) with efficiencies higher than 90%. These values are outstanding among organic thin film polymers for capacitor applications. The results and findings presented here pave the way to further increase the energy density of all-organic polymers and explore new candidates for advanced capacitors.

Scheme 1 shows general reaction procedures for the synthesis of the three designed polymers. The first polymer from the polythiourea family named PDTC-HK511 was prepared through addition reactions of *para*-phenylene diisothiocyanate (PDTC) and Jeffamine HK511. The second polymer in the polyurea family named TDI-EDR148 was prepared through addition reactions of toluene-2,4-diisocyanate (TDI) and Jeffamine EDR148. The third polymer from the polyimide family named BTDA-HK25 was prepared through addition reactions of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), Jeffamine HK511 and hexane-1,6-diamine (HDA). It was a copolymer of BTDA-HK511 and BTDA-HDA, where the molar ratio of BTDA-HK511 is 25%. BTDA-HK25 was chosen due to its balanced dielectric and thermal properties (see ESI†). Thin films were made with filtered polymer solution on a glass substrate using a film coater. As shown in Fig. S1,† the obtained polymer films were free-standing, 10–15 μm thick, and transparent. All polymers were characterized by ^{1}H NMR and FTIR to confirm the products of reactions (Fig. S2†). Thermal properties were also fully characterized (Fig. S3 & S4†) and the results are summarized in Table S1.†

The real and imaginary parts of the complex dielectric permittivity from broadband dielectric spectroscopy are shown in Fig. 1. At room temperature, all three polymers showed high dielectric constants above 4.5 and low dielectric loss factors below 0.02 at 1 kHz. PDTC-HK511 was shown to have a dielectric constant of around 5.8 with a loss factor of 0.012. TDI-EDR148 showed the highest dielectric constant of 6.6 and a loss factor of 0.018. BTDA-HK25 showed the lowest loss factor of less than 0.01 and a dielectric constant of 4.5 (Fig. S5†).

Strong sub-T_g relaxation loss peaks were observed as shown in Fig. 1b, d and f. The relaxation peak at high temperature related to the glass transition is α relaxation. The following relaxation peak is β relaxation which is related to crankshaft movements in polymer chains.[26] The γ relaxation peak at low temperature and high frequency is a result of local fluctuations of dipole vectors within a polymer chain. These observed β and



Scheme 1 Polymerization reaction scheme of three designed polymers: PDTC-HK511, TDI-EDR148 and BTDA-HK25.

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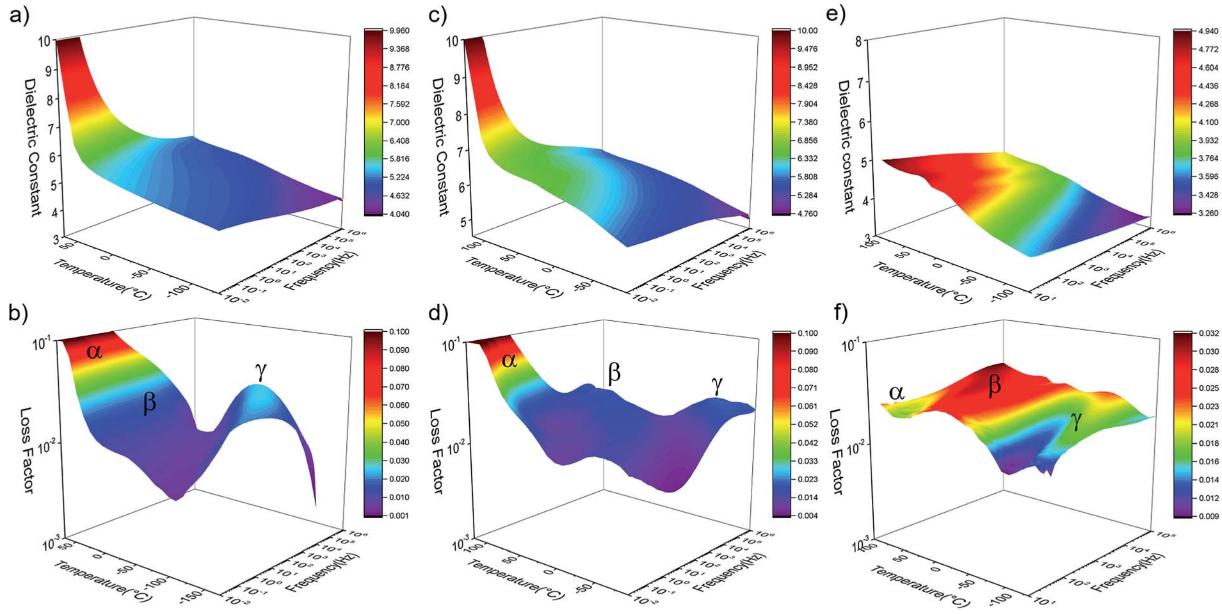

Fig. 1 Broadband dielectric spectroscopy as a function of wide ranges of temperatures and frequencies. The measurement results of the dielectric constant for (a) PDTC-HK511, (c) TDI-EDR148, and (e) BTDA-HK25, and the loss factor for (b) PDTC-HK511, (d) TDI-EDR148 and (f) BTDA-HK25.

γ relaxation peaks indicated strong localized dipole movement as a function of the applied field. The observed sub-T_g relaxation, especially the γ process, showed a high characteristic frequency according to the loss peak. This fast response polarization process came with a very small loss penalty for capacitors.

From Fig. 1a, c and e, we can see that the dielectric constant increased following each relaxation process according to the Kramer–Kronig relation.[27] The dielectric constant measured at −130 °C in each polymer was roughly the same as the machine learning predicted value on each base aromatic polymer without adding the flexible segments.[28] At such low temperature, dipolar polarization was "frozen" because of the solid-state energy barrier and the measured dielectric constant was all from electronic and atomic polarization. The contribution of each polarization process is given in Table 1 based on the refractive index measurement (see ESI page S7†). Dipolar polarization processes helped these designed polymers to enhance their dielectric constants more than 38% with increases larger than 1.5. Thus, the resulting dielectric constant of these designed polymers was higher than most polymers within their own class.[29–31]

Table 1 The breakdown of the dielectric constant into separate polarization processes

	$\varepsilon_{\text{electronic}}$	$\varepsilon_{\text{atomic}}$	$\varepsilon_{\text{dipolar}}$	$\varepsilon_{\text{total}}$	Dipolar enhancement[a]
PDTC-HK511	2.69	1.35	1.76	5.80	43.6%
TDI-EDR148	2.58	2.18	1.84	6.60	38.7%
BTDA-HK25	2.69	0.57	1.51	4.77	46.3%

[a] $\varepsilon_{\text{dipolar}}$ compared with $\varepsilon_{\text{electronic}} + \varepsilon_{\text{atomic}}$.

To shine more light on the correlation between the designed polymer structure and the dielectric polarization behavior, the activation energy of each relaxation process was extracted by using the Havriliak and Negami (HN) model as an indicator of the dipole rotation energy barrier.[32,33] According to the model, the peak frequency at each temperature point will follow the Arrhenius-type temperature dependence. The scaling behavior predicted by the Arrhenius equation with log(f) *vs.* 1/T will yield a straight line with a slope that is proportional to the activation energy. Fig. 2a shows the peak frequency *vs.* the reverse temperature plots according to the Arrhenius equation for all three polymers based on the dielectric spectroscopy measurement. Each data point corresponded to a relaxation peak frequency and fell into separate regions for β and γ relaxation. Each relaxation process followed a unique straight line, indicating Arrhenius type distribution. Linear curve fitting was performed, and the resulting activation energies of all sub-T_g relaxation processes are summarized in Fig. 2b. The activation energies for β relaxation were 0.38 eV, 0.25 eV and 0.32 eV for PDTC-HK511, TDI-EDR148 and BTDA-HK25, respectively. The activation energies for γ relaxation were 0.14 eV, 0.15 eV and 0.11 eV, respectively. Activation energies for both β and γ relaxation processes were similar in these polymers, indicating similar polarization behaviors. These activation energies were considered to be relatively low when compared with polypropylene, which had a value of 1.21 eV for β relaxation[16] and a value of 0.48 eV for γ relaxation.[34]

The low activation energy of each relaxation process indicated the movement freedom of the dipoles under an external field. The starting aromatic polar polymers had relatively high dielectric constants stemming from electronic and ionic polarization; however, their rigid structures with limited

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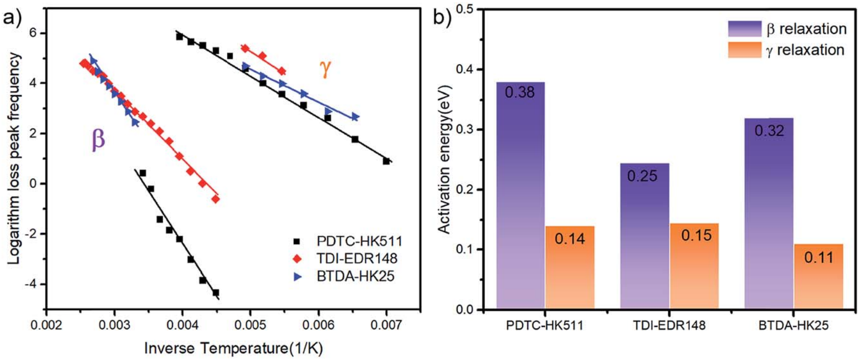

Fig. 2 (a) The temperature dependence of the loss peak maximum according to the Arrhenius equation. (b) Calculated activation energies for each sub-T_g relaxation process based on the Arrhenius equation.

movement freedom lead to weak dipolar polarization as dipoles could not rotate freely. The flexible segments added to the backbone gave the polymer chain extra flexibility for the local segment movement. These polar groups with orientational freedom were polarized under the external field and contributed to the overall dielectric constant. With the combination of rigid and flexible segments, free volume was created in the polymer and constraints on dipoles were reduced. Thus, this rotational freedom also contributed to a low dielectric loss factor.

The electrical energy storage capability of these polymers was studied under a high field with unipolar *D*–*E* loop measurements and the results are summarized in Fig. 3. High dielectric constants, high energy densities and high efficiencies were observed on all designed polymers. The apparent dielectric constant could be estimated from the slope of the charging loops and the values of 5.5 for PDTC-HK511, 6.4 for TDI-EDR148 and 4.5 for BTDA-HK25 agreed well with the dielectric measurement results in Fig. 1. All three polymers showed narrow *D*–*E* loops, and a breakdown strengths of up to 780 MV m^{-1} was achieved. These high breakdown strengths came from the selected rigid aromatic segments with large band gaps and the high dielectric constants could be attributed to the enhanced dipolar polarization.

The energy density and efficiency were calculated from the *D*–*E* loop results. The energy density obviously increased with the applied electric field and the efficiency decreased with the applied field as a result of conduction and other loss mechanisms. The maximum energy densities were 11 J cm^{-3}, 13 J cm^{-3}, and 12 J cm^{-3} for PDTC-HK511, TDI-EDR148, and BTDA-HK25, respectively, all with efficiencies above 90% at breakdown field. All polymers showed at least doubled energy

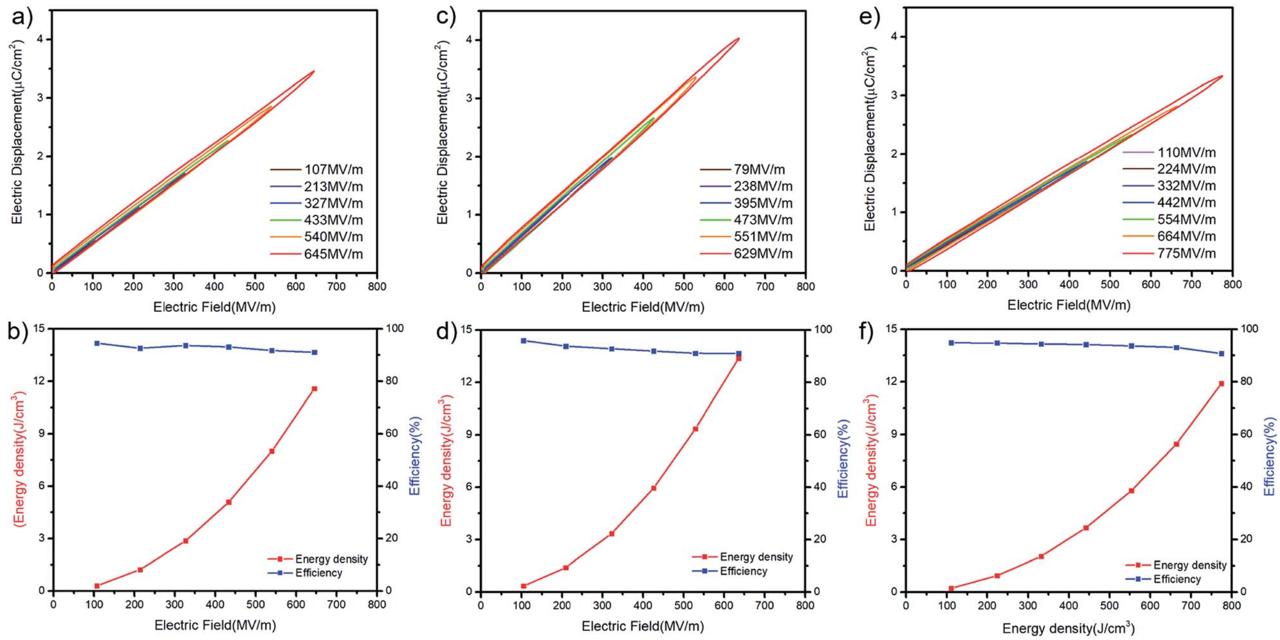

Fig. 3 High electric field *D*–*E* loop results. (a) *D*–*E* loops for PDTC-HK511 and (b) corresponding total energy density and efficiency. (c) *D*–*E* loops for TDI-EDR148 and (d) corresponding total energy density and efficiency. (e) *D*–*E* loops for BTDA-HK25 and (f) corresponding total energy density and efficiency.

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densities when compared to that of BOPP, with relatively high efficiencies. These values are outstanding among organic thin film polymers for capacitor applications.

Conclusions

In conclusion, we have introduced a novel molecular engineering design approach for high energy density and high efficiency polymers. Dipolar polarization was enhanced by combining rigid aromatic polymers with flexible segments in the polymer backbones. The aromatic segments provided a high band gap and high glass transition temperature, and the flexible segments gave dipoles the flexibility to rotate and created more free volume. Three polymers were synthesized based on this design methodology and free-standing films with large size were produced. These polymer films have enhanced dielectric constants (up to 45%) compared with their base polymers, with high energy densities of up to 13 J cm^{-3} and high efficiencies above 90%. Broadband dielectric spectroscopy showed multiple strong sub-T_g polarization processes with low activation energies compared with BOPP. These results confirmed the orientational flexibility of dipoles and the enhancement of dipolar polarization originating from the designed structure. With the designed molecular structure, the energy density and efficiency of these polymers were remarkably higher than those of other polymers within their own classes. These findings pave a way to further increase the energy density of organic polymers and explore novel high energy density polymers.

Conflicts of interest

There are no conflicts to declare.

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