

Metadielectric materials for energy storage

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Abstract: *Energy storage units having both high energy density and high power density are crucial for further development of technology. As the limitations of the electrochemical batteries are impossible to overcome, the right answer should arrive from simpler devices and capacitor is the simplest. We show that high energy density can be achieved using layers of organic molecules with large second-order permittivity. Molecular polarizabilities and hyperpolarizabilities are calculated for various molecules using quantum chemistry software, and the expressions related them to macroscopic permittivities are derived. We believe that the proposed approach provides new opportunities for design of the energy storage devices.*

Keywords: energy storage; conjugated polymers; polarizability; hyperpolarizability; electron donors and acceptors.

Introduction: Energy Storage

Efficient energy storage is the key component in the development of various modern technologies. In the present time, the all-electric cars start to enter the vehicle market but they are still more expensive and less trustworthy than the usual ones. Electronic devices, which are omnipresent in modern society, are also heavily dependent on reliable energy storage modules. Moreover, renewable energy sources such as solar cells and wind turbines are sustainable and environmentally friendly, but their energy production is intermittent and the effective storage would make the energy available on demand. In the present time, the main storage devices are the batteries. The energy is stored electrochemically, i. e. carriers released in chemical reactions can enter electrical circuits. The energy density of batteries is very high and they are relatively cheap. During the charging process, the carriers (like lithium ions) are returned back to the source. This process is slow and, moreover, it degrades the battery material. Thus, the power density of the batteries is low and their lifetime is short due to the material damage. Furthermore, the batteries become less reliable at elevated temperatures. The alternative storage units are capacitors, where the energy is stored electrostatically [1]. The charging process is fast, leading to the high power density and the longtime reliability. The main shortcoming for capacitors is their low energy density. In order to overcome it, novel devices called supercapacitors have been developed [2]. They have the energy densities

greater than those of conventional capacitors and power densities greater than those of batteries. However, there is still no structure having the power density comparable to standard capacitors and the energy density comparable to batteries [1]. Moreover, the cost of supercapacitors remains relatively high.

Introduction: Conjugated Supramolecules

In the present paper, we propose to use the conjugated supramolecules with large second-order permittivity to develop capacitors with high energy density and high power density. Conjugated supramolecules are molecular stacks with repeating units of fundamental monomers.

We propose to use aromatic molecules as our fundamental monomers. They are expected to have high polarizability and even exhibit metallic conductivity [3]. Accordingly, they are shown to have a high dielectric constant up to 2.0×10^5 (at 1 kHz) [4,5]. So large value is most probably due to the hyperelectronic polarization, which is the analog of the space-charge polarization in doped semiconductors. Certain electrons can be detached from the host atom and moved over to the other side of the molecule creating a large polarizability. The polarizability shows a non-linear dependence on the electric field and its magnitude is several orders larger than that of the electronic polarization, especially in the frequency range of kHz-MHz, which makes such systems most suitable for the energy storage purposes because its contribution is the largest at the static fields. Similar molecules were shown to exhibit strong non-linear optical properties [6] and, correspondingly, we can expect large hyperpolarizabilities in these structures.

The conduction can compromise the high dielectric strength of the dielectric. To avoid this, we propose to couple the aromatic molecules with high polarization to aliphatic alkyl tails having high resistance. The example of such molecules is shown in Fig.1. Growth of similar structures was discussed in Refs. [7,8]. Such combination naturally leads to the layered arrangement, with alternate layers having high permittivity and high breakdown voltage.

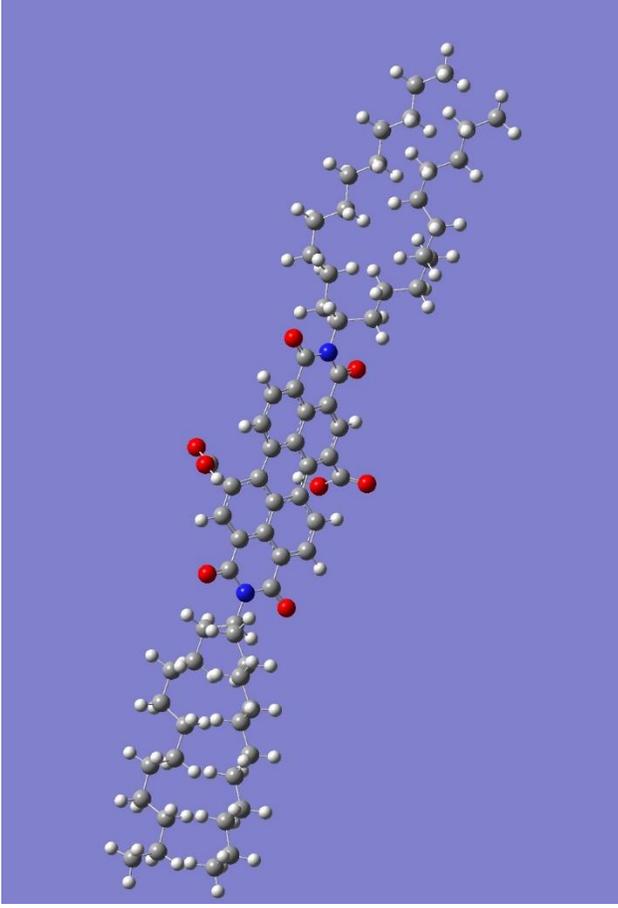


Figure 1. Molecular design for high energy density capacitors. Aromatic core with high polarizability is attached to alkyl tails with high resistance

Theory: Energy Density of Nonlinear Capacitors

The energy density of electric field is given by [9]

$$w = \int_0^D \vec{E} \cdot d\vec{D}' = \vec{E} \cdot \vec{D} - \int_0^E \vec{D} \cdot d\vec{E}'. \quad (1)$$

For simplicity, we consider the isotropic and uniform situation with all the fields directed along the x -axis. In this case, for the nonlinear media the electric displacement can be written as

$$D = \varepsilon_0 \varepsilon^{(1)} E + \varepsilon_0 \varepsilon^{(2)} E^2 + \dots \quad (2)$$

Substituting Eq. (2) into Eq. (1), we obtain for the energy density

$$w = \varepsilon_0 \varepsilon^{(1)} \frac{E^2}{2} + \varepsilon_0 \varepsilon^{(2)} \frac{2E^3}{3} + \dots \quad (3)$$

For the flat-plate capacitor with the plate area A , plate separation d , applied voltage $V_{op} = E/d$, and linear capacitance without dielectric $C_0 = \varepsilon_0 A/d$, the total stored energy is

$$\begin{aligned} W &= \int w dVol = \varepsilon^{(1)} C_0 \frac{V_{op}^2}{2} + \varepsilon^{(2)} C_0 \frac{2V_{op}^3}{3d} + \dots \\ &= \varepsilon_{eff} C_0 \frac{V_{op}^2}{2} \end{aligned} \quad (4)$$

where

$$\varepsilon_{eff} = \varepsilon^{(1)} + \frac{4V_{op}}{3d} \varepsilon^{(2)} + \dots \quad (5)$$

Thus, one can see that the dielectric with large second-order permittivity can be used for the heavy-duty capacitors especially if they are charged at large voltages.

Theory: Linear and Nonlinear Clausius-Mossotti Relations

Linear and nonlinear permittivities can be determined using the generalization of the Clausius–Mossotti relation in terms of polarizability and hyperpolarizability (second-order polarizability). Macroscopic polarization is given by $P = N p_{ind}$,

$$P = D - \varepsilon_0 E = \varepsilon_0 (\varepsilon^{(1)} - 1) E + \varepsilon_0 \varepsilon^{(2)} E^2 + \dots \quad (7)$$

In the simplest Lorentz approximation, the induced dipole can be expressed in terms of the local field

$$E_{loc} = E + \frac{P}{3\varepsilon_0}, \quad (8)$$

as

$$p_{ind} = \alpha E_{loc} + \beta E_{loc}^2 + \dots, \quad (9)$$

where α and β are the polarizability and hyperpolarizability, respectively. In the capacitor structure, the external field will be applied along the main direction of the molecule, so $\alpha = \alpha_{xx}$ and $\beta = \beta_{xxx}$. Substituting Eqs. (8) and (9) into Eq. (6) and comparing to Eq. (7), we can equalize the coefficients with the same power of the electric field E . The linear term would give as the usual Clausius–Mossotti relation

$$\frac{(\varepsilon^{(1)} - 1)}{(\varepsilon^{(1)} + 2)} = \frac{N\alpha}{3\varepsilon_0}, \quad (10)$$

whereas the quadratic term would provide the expression for the second-order permittivity, as

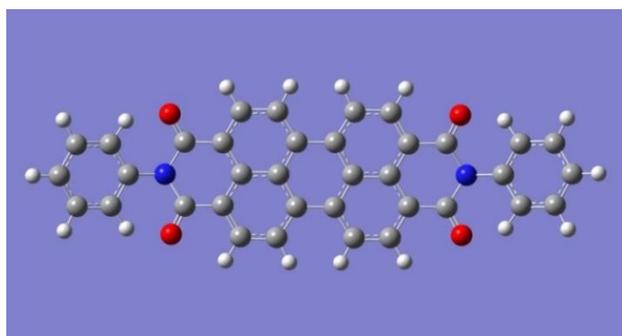
$$\varepsilon^{(2)} = \frac{N\beta}{3\varepsilon_0} \left(\varepsilon^{(1)} + 2 \right) \left(1 + \frac{2}{3} (\varepsilon^{(1)} - 1) + \frac{1}{9} (\varepsilon^{(1)} - 1)^2 \right). \quad (11)$$

Here, N is the density of molecules. Thus, having the values for α and β it is possible to determine the first- and

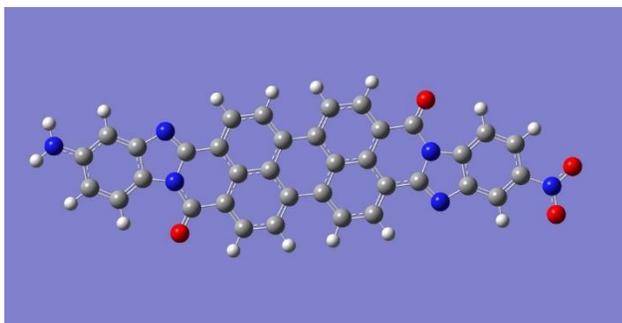
second-order permittivities and, correspondingly, the energy stored in the nonlinear capacitor.

Results

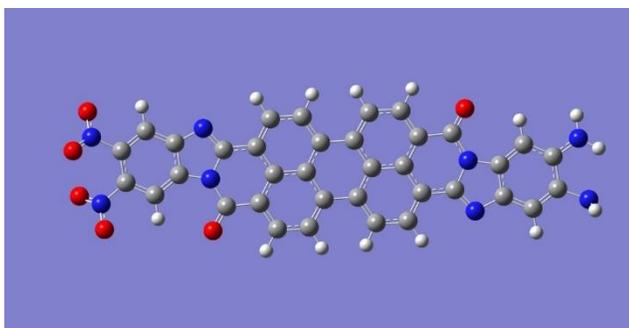
Proper molecular design is crucial for the achievement of high-polarizability structures. Using the Langhals perylene (LP) molecule, Fig. 2(a), as example of molecule with shorter conjugated system, we used extended conjugation of amidines with electron acceptor group NO₂ and electron donor group NH₂ to compare polarizabilities. In Fig. 2 (b), we show the structure with the single acceptor and donor groups at the apex positions (NAP_1), while in Fig 2 (c) the hypothetical structure with the double groups is presented (NAP_2). Comparison of NAP_1 and NAP_2 allows us to get deeper insight on the dependence of the polarizabilities on the number of donors and acceptors.



a)



b)



c)

Figure 2. (a) Langhals perylene; (b) Phenyl-perylene with the single NO₂ and NH₂ groups at the apex positions; (c) Phenyl-perylene with the double NO₂ and NH₂ groups. Carbon, hydrogen, nitrogen, and oxygen atoms are shown by grey, white, blue, and red colors, respectively.

These molecules are analyzed with Gaussian09 software [10], their polarizabilities and hyperpolarizabilities are determined using the B3LYP method with 6-31G basic sets and are given in Table 1. They are expressed in atomic units, $1 \text{ a.u.} = e^2 a_0^2 / E_h$ for α and $1 \text{ a.u.} = e^3 a_0^3 / E_h^2$ for β , where e is the electron charge, a_0 is the Bohr radius, and E_h is the Hartree energy.

Table 1. Polarizabilities and hyperpolarizabilities for the molecules of Fig. 2

	LP	NAP_1	NAP_2
α	945	1252	1546
β	0.041	21106	119078

One can see that while the polarizabilities of these molecules are comparable, the hyperpolarizabilities are increased by several orders of the magnitude by the introduction of the donor/acceptor groups. It should be also noted that the doubling of these groups increases the hyperpolarizability by the factor of 5.

The values for the microscopic molecular polarizabilities can be recalculated to the macroscopic permittivities using Eqs. (10) and (11). However, linear Clausius-Mossotti expression, Eq. (10), would not provide accurate results at high molecular density of conjugated polymers because of so-called “polarization catastrophe”, which happens when the right side of Eq. (10) becomes close to one [11]. To avoid these complications, we use the linear permittivity as a parameter to calculate the second-order permittivity, Eq. (11) and the effective permittivity, Eq. (5), involved in the expression for the energy density. From practical point of view, $\epsilon^{(1)}$ can be understood as a dielectric constant at zero applied voltage and obtained values of ϵ_{eff} would provide the dielectric constant for the operation voltage of the capacitor. In Fig. 3 we show the dielectric constants for NAP_1 and NAP_2 as functions of the zero-field values at electric field $V/d = 1 \text{ V/nm}$ and the molecular density $N = 3 \cdot 10^{27} \text{ m}^{-3}$. It is clear that the low value of the hyperpolarizability for LP makes its dielectric constant independent on the applied voltage.

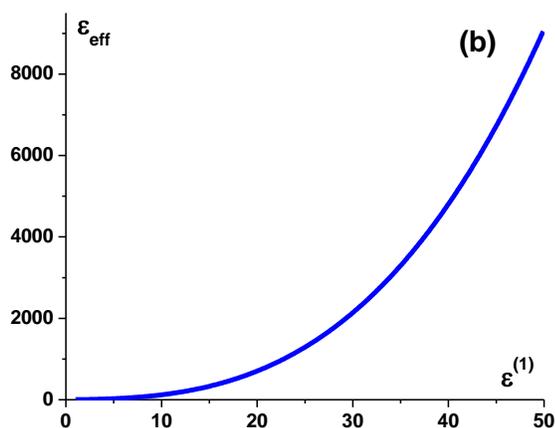
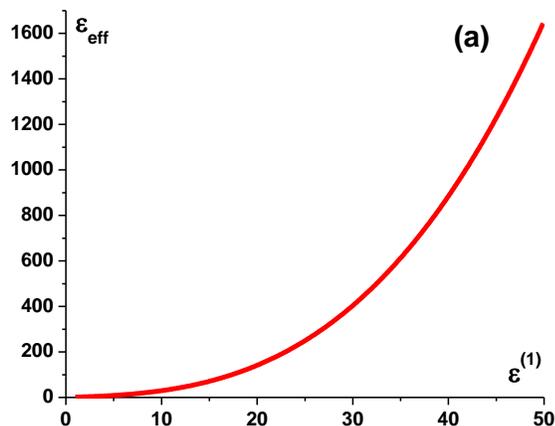


Figure 3. Dependence of the dielectric constant for the capacitor operation voltage on its zero-voltage value for (a) NAP_1 and (b) NAP_2.

One can see from this figure that even for the moderate values of the dielectric constant at zero applied voltage, the effective permittivity at operational voltages can reach very large values, which makes these structures very attractive for the energy storage applications. The reason for this phenomenology is the giant nonlinear response of these molecules to external electric field.

Conclusions

In conclusions, we propose to explore organic molecules with large second-order permittivity for the energy storage devices. Actual device would have a multilayer structure with alternate layers of the materials with high permittivity and high breakdown voltage. We derive the contributions of the second-order permittivity to the energy stored in the capacitor. The values of molecular polarizabilities and hyperpolarizabilities are calculated using the quantum chemistry software, Gaussian09. We show that introducing

the electron acceptor group NO_2 and the electron donor group NH_2 to the molecule of perylene, it is possible to increase the hyperpolarizability even if the polarizability remains essentially the same. The obtained values are used to determine the first- and second-order permittivities, as well as the effective dielectric constant involved in the expression for the energy density. We show that for our perylene-based molecules, the effective dielectric constant at the operational voltage is quite high, which allows us to use the proposed structures for the energy storage device applications.

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