

# Quadrupole versus Dipole Brownian Photomotors

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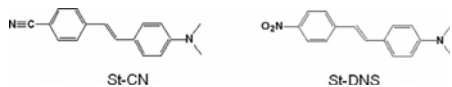
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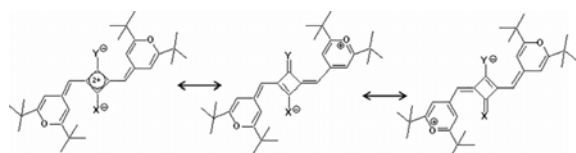
**Background and purpose of the work** The operation of all Brownian motors, which rectify chaotic Brownian motion into directed transport of particles [1], is based on a general principle, namely, for a nanoparticle (or a large molecule) to move directionally, it must exist in at least two alternating states, while the potential energy of the particle must be spatially asymmetric in at least one of them. If states are switched by light, then the corresponding nanodevices belong to the class of Brownian photomotors [2]. In the model of a near-surface Brownian photomotor developed by us earlier [3], cyclic photoexcitation causes fluctuations of the dipole, quadrupole, and higher multipole moments of the molecule. Their contributions to the motor properties can be controlled by selecting suitable substrates according to the established symmetry laws [4].

It is of interest to study molecules in which fluctuations involve only even-order (charge, quadrupole moment, etc.) or only odd-order multipole moments (dipole, octupole moment, etc.), since the corresponding photomotors should differ greatly from each other in symmetry-related properties [5]. Previously, we considered the model of dipole photomotors, in which only the dipole moment of the molecule fluctuates [2]. The purpose of this work is (i) to study their quadrupole analogs, i.e., photomotors based on uncharged molecules interacting with an external periodic asymmetric electric field only through quadrupole moment fluctuations and (ii) to compare symmetry properties and operating characteristics of dipole and quadrupole photomotors.

## Objects and methodology

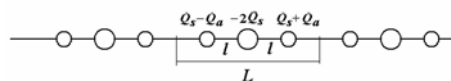


**Scheme 1.** Donor-acceptor stilbenoids as dipole photomotors (uncharged, dipole moment changes significantly on excitation).



**Scheme 2.** Symmetric pyrrolo-4(thio)squaraines, **Sq-OO** (X=Y=O), **Sq-SS** (X=Y=S), and **Sq-OS** (X=O, Y=S), as quadrupole photomotors (uncharged, dipole moment is zero, quadrupole moment changes significantly on excitation).

As a simple model of the polar substrate for such photomotors, we use a one-dimensional chain with a linear density  $\rho(x)$  of periodically distributed charge (Fig. 1).



**Fig. 1.** A model periodic substrate with three potential-generating atoms in the unit cell ( $Q_s$  and  $Q_a$  are symmetric and antisymmetric contributions to the atomic charges,  $L$  is a spatial period of charge distribution,  $l$  is the separation between adjacent atoms).

The average velocity of an individual motor with a molecule moving along the longitudinal axis  $x$  of the system (coinciding with the molecular axis) at the distance  $z$  from the substrate was determined by the equation

$$\langle v \rangle = -\frac{D}{L} \frac{16\pi(1-\varepsilon^2)Z}{(k_B T)^3 (1+4Z)^2 (1+Z)} \text{Im} \left[ (1+4Z)u_1 w_1 w_2^* + 2(1+Z)w_1^* w_2^* + 6\varepsilon Z w_1^* w_2^* \right] \quad (1)$$

where  $D = k_B T / \zeta$  is the diffusion coefficient (with  $k_B$  denoting the Boltzmann constant,  $T$  the equilibrium absolute temperature, and  $\zeta$  the friction coefficient);  $Z = \Gamma L^2 / [(4p)^2 D]$  is a dimensionless parameter depending on the laser operating regime (through  $\Gamma = 1/\tau_+ + 1/\tau_-$ , where  $\tau_+$  and  $\tau_-$  are the pulse and dark phase durations) and temperature (through  $D$ );  $\varepsilon = (\tau_+ - \tau_-) / \tau$ ;  $u_q = \rho_q K_0(|k_q z|) (R_q^{(+)} + R_q^{(-)})$ ,  $w_q = \rho_q K_0(|k_q z|) (R_q^{(+)} - R_q^{(-)})$ , where  $K_0(z)$  is the Macdonald function,  $k_q = 2\pi q/L$  ( $q$  is an integer,  $L$  is a spatial period of charge distribution),  $\rho_q = L^{-1} \int dx \rho(x) e^{ik_q x}$  is the Fourier component of the charge density  $\rho(x)$

on the substrate;  $q = \pm 1, \pm 2$ , and  $R_q^{\pm} = \sum p_j^{\pm} e^{ik_q x_j^{\pm}}$  is a single molecular parameter determined by the set of atomic charges  $p_j$  and coordinates  $x_j$ .

The corresponding average velocity of molecules in a collective motor is found as

$$\langle v \rangle = -\frac{D}{L} \frac{16\pi(1-\varepsilon^2)Z}{(k_B T)^3 (1+4Z)^2 (1+Z)} K_0^2(|k_1 z|) K_0^2(|k_2 z|) \left[ 2\rho_{s1} \rho_{s2} \rho_{a1} - (\rho_{s1}^2 - \rho_{a1}^2) \rho_{a2} \right] \times$$

$$\times \left[ (1+4Z) \langle R_1 \Delta R_1 \Delta R_2^* \rangle + 2(1+Z) \langle \Delta R_1^2 R_2^* \rangle + 6\varepsilon Z \langle \Delta R_1^2 \Delta R_2^* \rangle \right], \quad (2)$$

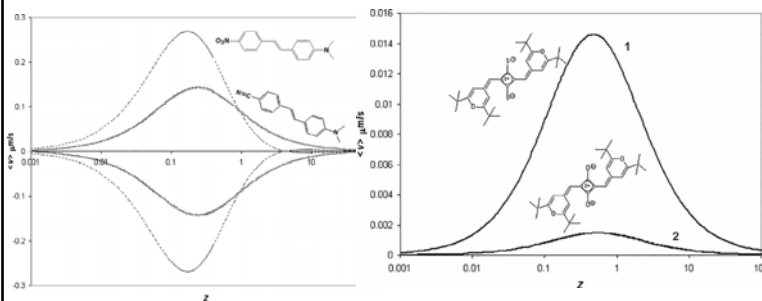
$$\langle R_1 \Delta R_1 \Delta R_2^* \rangle = R_{s1} (\Delta R_{s1} \Delta R_{s2} + \Delta R_{a1} \Delta R_{a2}) + R_{a1} (\Delta R_{s1} \Delta R_{a2} - \Delta R_{a1} \Delta R_{s2}),$$

$$\langle \Delta R_1^2 R_2^* \rangle = R_{s2} (\Delta R_{s1}^2 - \Delta R_{a1}^2) + 2R_{a2} \Delta R_{s1} \Delta R_{a1}, \quad \langle \Delta R_1^2 \Delta R_2^* \rangle = \Delta R_{s2} (\Delta R_{s1}^2 - \Delta R_{a1}^2) - 2\Delta R_{a2} \Delta R_{s1} \Delta R_{a1},$$

$$R_q = R_q^+ + R_q^- \equiv R_{sq} + iR_{aq}, \quad \Delta R_q = R_q^+ - R_q^- \equiv \Delta R_{sq} + i\Delta R_{aq}, \quad \rho_q \equiv \rho_{sq} + i\rho_{aq}$$

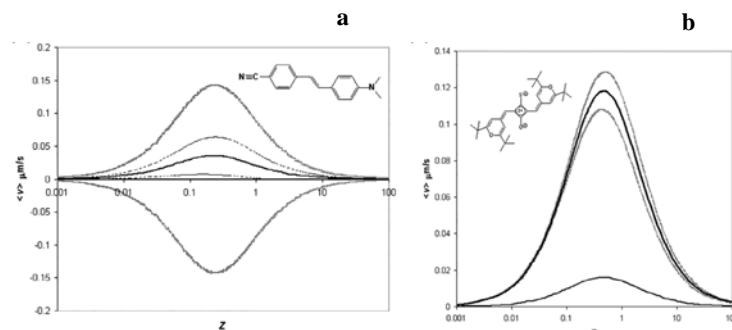
(Eq. (2) includes previously denoted quantities [3], as well as symmetric ( $s$ ) and antisymmetric ( $a$ ) contributions to the charge distributions in the molecule and substrate).

## Results



**Fig. 2.** The average velocities of directed motion of two individual oppositely oriented molecules, **St-DNS** (dashed lines) and **St-CN** (gray filled lines), and of the corresponding molecular ensembles (two solid lines merged with the abscissa) versus the parameter  $Z$  (proportional to the laser-induced frequency of potential fluctuations and to the reciprocal temperature) on the symmetric substrate ( $Q_s = 0.5, Q_a = 0$ ).

**Fig. 3.** The average velocities of directed motion of two individual oppositely oriented molecules and of the molecular ensemble for **Sq-SS** (merged line triad 1) and the same for **Sq-OO** (merged line triad 2) versus the parameter  $Z$  on the antisymmetric substrate ( $Q_s = 0, Q_a = 0.5$ ).



**Fig. 4.** The average velocities of directed motion of two individual oppositely oriented molecules and of the molecular ensemble plotted versus the parameter  $Z$ : (a) – for **St-CN** as a purely dipole photomotor on the symmetric substrate ( $Q_s = 0.5, Q_a = 0$ , gray-filled abscissa-symmetric lines and solid line merged with the abscissa) and as a dipole photomotor with a quadrupole admixture on the asymmetric substrate ( $Q_s = 0.5, Q_a = 0.45$ , dashed lines and the intermediate solid line); (b) – for **Sq-OS** as a purely quadrupole photomotor on the antisymmetric substrate ( $Q_s = 0, Q_a = 0.5$ , merged line triad at the bottom) and as a quadrupole photomotor with a dipole admixture on the asymmetric substrate ( $Q_s = 0.45, Q_a = 0.5$ , gray filled lines and the intermediate solid line at the top)

**Conclusions** 1) Purely dipole photomotors can operate only on substrates with symmetric charge distribution and their ensemble with random molecular orientations undergoes equidirectional diffusion rather than directed motion.

2) Purely quadrupole photomotors need substrates with antisymmetric charge distribution for directed motion to occur and they can move directionally in an ensemble.

3) Quadrupole photomotors provide much smaller velocities of directed motion than their dipole counterparts (as a result of the much weaker interaction of quadrupoles than dipoles with an electric field).

4) The model used affords the rational design of photomotors both by the selection of appropriate moving molecules and by the continuous wide-range tuning of charge-distribution symmetry in substrates.

5) The most promise in photomotor design is shown not by purely dipole or purely quadrupole molecules but by those of mixed nature, in combination with appropriately adjusted asymmetric substrates.

**References** 1. P. Reimann, Phys. Rep. **361**, 57 (2002). 2. M. L. Dekhtyar, A. A. Ishchenko, V. M. Rozenbaum, J. Phys. Chem. B **110**, 20111 (2006). 3. M. L. Dekhtyar, V. M. Rozenbaum. J. Chem. Phys. **134**, 044136 (2011). 4. M. L. Dekhtyar, V. M. Rozenbaum. MATCH Commun. Math. Comput. Chem. **71**, 609 (2014). 5. M. L. Dekhtyar., V. M. Rozenbaum J. Chin. Chem. Soc. **70**, 460 (2023).