A Theoretical Study of the Optimal Design of a UV-controllable Smart Surface Decorated by a Hybrid Azobenzene-containing Polymer Layer

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Supporting Information

Model and theory



Figure S1: The sketch map of the grafting points on the nanoparticle and the surface. This sketch has two parts. One is an impenetrable planar surface with grafting points which are arranged on a hexagonal lattice, and the other is a freely moving hard sphere with grafting points. The grafting density of the planar and the sphere can be controlled by lattice constant c and c_{nano} , which was not changed in present study.

Consider an impenetrable planar surface coated with a hybrid polymer layer, which is composed of n_{azo} azo-polymers with reactive end-group as the receptors and n_{homo} homopolymers. The grafting points on the surface are arranged according to the hexagonal symmetry shown in Fig. S1. The grafting density can be controlled by the lattice constant c, which is unchanged in present study. The contour length of the azo-polymer is L, which is regarded as the length unit in present work. An azo-bond locates at the position L_{azo} along its backbone measured from the grafting point and $f \equiv L_{azo}/L$ denotes its relative position. To model the photoisomerization of the azo-bond, its bond angle γ_{azo} is set to two values, i.e., 180° and 60° , which correspond to the *trans* and *cis* conformations, respectively. Each homopolymer has the contour length of L_{homo} and $f_{\text{homo}} \equiv L_{\text{homo}}/L$ denotes its relative length. A freely moving hard sphere with radius r_0 and coated by n_{lig} ligand polymers is used to model the spherical nanoparticle or anything alike in experiments. Each ligand polymers has contour length L_{lig} and $f_{\text{lig}} \equiv L_{\text{lig}}/L$ denotes its relative length. All end-groups of the ligand polymers can react with the end-groups of the azo-polymers. The panels (a) and (b) of Fig. 1 in the main body of the paper present the surface under UV off and on conditions, respectively. Accordingly, azo-polymers can take *trans*-isomer or *cis*-isomer, which make the nanoparticle adsorbed on the substrate or erased, respectively.

The wormlike chain (WLC) model is adopted to describe the polymers both on the nanoparticle and on the planar substrate. It is assumed that all the polymers have the same persistence length l_p . The configuration of the semiflexible chain is characterized by a continuous space curve $\mathbf{R}(s)$ and its tangent vector $\mathbf{u}(s)$, corresponding to the spatial position vector and the unit tangent vector for a particular polymer segment s, respectively, where s denotes the contour variable of the segment. A given chain configuration is subject to the Hamiltonian,

$$\beta \mathcal{H}_0[\mathbf{u}(s)] = \frac{1}{4(L/a)} \int_0^1 \mathrm{d}s \left| \frac{\mathrm{d}\mathbf{u}(s)}{\mathrm{d}s} \right|^2 \tag{1}$$

where the tangent vector

$$\mathbf{u}(s) = \frac{1}{L} \frac{\mathrm{d}\mathbf{R}(s)}{\mathrm{d}s},\tag{2}$$

and $a = 2l_p$. Parameter L/a characterizes the chain stiffness. The larger L/a is, the more flexible the chain is. Note that all the lengths are scaled by L and energy is scaled by $\beta^{-1} = k_B T$, with k_B and T being the Boltzmann constant and the absolute temperature, respectively.

The probability functions for a given configuration of the jth azo-polymer and the ho-

mopolymer on the planar surface are

$$P_{\rm azo}^{j} \left[\mathbf{R}_{\rm azo}^{j}(s), \mathbf{u}_{\rm azo}^{j}(s) \right] \propto \exp\{-\beta \mathcal{H}_{0}[\mathbf{u}_{\rm azo}^{j}(s)]\} \delta \left[\mathbf{R}_{\rm azo}^{j}(0) - \tilde{\mathbf{R}}_{\rm I}^{j} \right] \delta(\gamma_{\rm azo} - \alpha) \\ \times \prod_{s} \left\{ \delta \left[|\mathbf{u}_{\rm azo}^{j}(s)| - 1 \right] \delta \left[\mathbf{u}_{\rm azo}^{j}(s) - \frac{1}{L} \frac{\mathrm{d}\mathbf{R}_{\rm azo}^{j}(s)}{\mathrm{d}s} \right] \right\}, \quad (3)$$

and

$$P_{\text{homo}}^{j} \left[\mathbf{R}_{\text{homo}}^{j}(s), \mathbf{u}_{\text{homo}}^{j}(s) \right] \propto \exp \left\{ -\beta \mathcal{H}_{0} \left[\mathbf{u}_{\text{homo}}^{j}(s) \right] \right\} \delta \left[\mathbf{R}_{\text{homo}}^{j}(0) - \tilde{\mathbf{R}}_{\text{I}}^{j} \right] \\ \times \prod_{s} \left\{ \delta \left[|\mathbf{u}_{\text{homo}}^{j}(s)| - 1 \right] \delta \left[\mathbf{u}_{\text{homo}}^{j}(s) - \frac{1}{L} \frac{\mathrm{d}\mathbf{R}_{\text{homo}}^{j}(s)}{\mathrm{d}s} \right] \right\} (4)$$

respectively. The first Dirac δ function constrains the grafting location $\tilde{\mathbf{R}}_{\mathbf{I}}^{j}$ of the *j*th chain on the surface. The grafting points $\{\tilde{\mathbf{R}}_{\mathbf{I}}^{j}\}$ follow the hexagonal symmetry as shown in Fig. S1. The second δ function models the photoactivity of the azo-group. The last two Dirac delta functions ensure the finite extensibility constraint of the chain and introduce the dependence of $\mathbf{R}(s)$ on $\mathbf{u}(s)$. Similarly, the probability function for a given configuration of the *j*th ligand polymer on the nanoparticle is

$$P_{\text{lig}}^{j} \left[\mathbf{R}_{\text{lig}}^{j}(s), \mathbf{u}_{\text{lig}}^{j}(s) \right] \propto \exp\{-\beta \mathcal{H}_{0}[\mathbf{u}_{\text{lig}}^{j}(s)]\} \delta \left[\mathbf{R}_{\text{lig}}^{j}(0) - \tilde{\mathbf{R}}_{\text{II}}^{j} \right] \\ \times \prod_{s} \left\{ \delta \left[|\mathbf{u}_{\text{lig}}^{j}(s)| - 1 \right] \delta \left[\mathbf{u}_{\text{lig}}^{j}(s) - \frac{1}{L} \frac{\mathrm{d}\mathbf{R}_{\text{lig}}^{j}(s)}{\mathrm{d}s} \right] \right\}$$
(5)

where $\tilde{\mathbf{R}}_{\text{II}}^{j}$ is the position of the grafting point of the *j*th ligand polymer on the nanoparticle surface. The spherical surface is spatially discretized with triangular lattices.¹ Specifically, the spherical surface is firstly discretized into triangular grids generated by the spherical projection of the regular icosahedron. When the midpoints of three edges with geodesic arcs are connected by a line, each of the 20 triangular faces is subdivided into four, yielding 80 smaller triangles which have 42 vertices in total. In this work, these vertices are chosen as $\tilde{\mathbf{R}}_{\text{II}}^{j}$. The variation of the position vectors characterizes the translational and rotational degrees of freedom of the nanoparticle.

The excluded volume interactions between polymer segments are described as

$$\beta V_1(\mathbf{r}, \mathbf{r}') = \kappa \delta(\mathbf{r} - \mathbf{r}'). \tag{6}$$

The attractive interaction between the ligand and receptor is given by

$$\beta V_2(\mathbf{r}, \mathbf{r}') = -\tau \delta(\mathbf{r} - \mathbf{r}'). \tag{7}$$

To model the impenetrable surface of the spherical particle and the planar surface, an external potential is imposed

$$\beta V_3(\mathbf{r}) = \begin{cases} 0, & |\mathbf{r} - \mathbf{r}_c| > r_0 \quad \text{or} \quad z \le z_0 \\ \infty, & |\mathbf{r} - \mathbf{r}_c| < r_0 \quad \text{or} \quad z > z_0 \end{cases}$$
(8)

where \mathbf{r}_c is the center position of the nanoparticle and z is the z-component of position vector \mathbf{r} . The substrate is set at the x - y plane as shown in Fig. S1. To characterize the structure of the system, we define the total density operator of segments

$$\hat{\rho}(\mathbf{r}) = \frac{1}{\rho_0} (L/a) \sum_{k=1}^{n_{\text{azo}}} \int_0^1 \mathrm{d}s \delta \left[\mathbf{r} - \mathbf{R}_{\text{azo}}^j(s) \right] + \frac{1}{\rho_0} (L/a) \sum_{k=1}^{n_{\text{homo}}} \int_0^{f_{\text{homo}}} \mathrm{d}s \delta \left[\mathbf{r} - \mathbf{R}_{\text{homo}}^j(s) \right] + \frac{1}{\rho_0} (L/a) \sum_{k=1}^{n_{\text{lig}}} \int_0^{f_{\text{lig}}} \mathrm{d}s \delta \left[\mathbf{r} - \mathbf{R}_{\text{lig}}^j(s) \right]$$
(9)

and the density operators of the ligand and the receptor are respectively defined by

$$\hat{\rho}_{\text{lig,end}}(\mathbf{r}) = \frac{1}{\rho_0} \sum_{j=1}^{n_{\text{lig}}} \delta\left[\mathbf{r} - \mathbf{R}_{\text{lig}}^j(f_{\text{lig}})\right], \qquad (10)$$

and

$$\hat{\rho}_{\text{azo,end}}(\mathbf{r}) = \frac{1}{\rho_0} \sum_{j=1}^{n_{\text{azo}}} \delta\left[\mathbf{r} - \mathbf{R}_{\text{azo}}^j(1)\right], \qquad (11)$$

Here, ρ_0 is the bulk density of the monomers.

The partition function of the whole system is given by

$$\mathcal{Z} \simeq \int \prod_{\alpha,j} \{ \mathcal{D}[\mathbf{R}^{j}_{\alpha}(s), \mathbf{u}^{j}_{\alpha}(s)] P^{j}_{\alpha}[\mathbf{R}^{j}_{\alpha}(s), \mathbf{u}^{j}_{\alpha}(s)] \} \\ \times \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}(\mathbf{r}) \beta V_{\mathrm{I}}(\mathbf{r}, \mathbf{r}') \hat{\rho}(\mathbf{r}') - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}(\mathbf{r}) \beta V_{\mathrm{II}}(\mathbf{r}, \mathbf{r}') \hat{\rho}(\mathbf{r}') - \int d\mathbf{r} \beta \mathcal{H}_{I}(\mathbf{r}) \hat{\rho}(\mathbf{r}) \right\} \\ = \int \mathcal{D}\{\Omega, \eta\} \exp \{-\beta \mathcal{F}[\Omega, \eta]\}$$
(12)

where we have performed the Hubbard-Stratonovich transformation to decouple the selfinteraction of the density field $\hat{\rho}(\mathbf{r})$, resulting in the introduction of a potential field $\Omega(\mathbf{r})$ coupling to $\hat{\rho}(\mathbf{r})$ and potential fields $\eta_{I,II}(\mathbf{r})$ coupling to $\hat{\rho}_{I,II}(\mathbf{r})$, respectively. The final line defines the effective Hamiltonian of the system

$$\beta \mathcal{F}[\Omega] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \Omega(\mathbf{r}) [\beta V(\mathbf{r}, \mathbf{r}')]^{-1} \Omega(\mathbf{r}') + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \eta_{\mathrm{I}}(\mathbf{r}) [\beta V_{\mathrm{II}}(\mathbf{r}, \mathbf{r}')]^{-1} \eta_{\mathrm{II}}(\mathbf{r}') - \int d\mathbf{r} \beta \mathcal{H}_{I}(\mathbf{r}) \rho(\mathbf{r}) - \sum_{j=1}^{n_{\mathrm{azo}}} \ln Q_{\mathrm{azo}}^{j}[\Omega, \eta_{\mathrm{II}}] - \sum_{j=1}^{n_{\mathrm{homo}}} \ln Q_{\mathrm{homo}}^{j}[\Omega] - \ln Q_{\mathrm{nano}}[\Omega, \eta_{\mathrm{I}}],$$
(13)

where the single-chain partition function of the jth azo and ligand polymer are

$$Q_{\text{azo}}^{j}[\Omega,\eta_{\text{II}}] = \int \{\mathcal{D}[\mathbf{R}_{\text{azo}}^{j}(s),\mathbf{u}_{\text{azo}}^{j}(s)] \exp\left\{-\beta\mathcal{H}_{0}[\mathbf{u}_{\text{azo}}^{j}(s)] - \int_{0}^{1} \mathrm{d}s\omega[\mathbf{R}_{\text{azo}}^{j}(s)] + \eta_{\text{II}}\left[\mathbf{R}_{\text{azo}}^{j}(1)\right]\right\} \times \delta\left[\mathbf{R}_{\text{azo}}^{j}(0) - \tilde{\mathbf{R}}_{\text{I}}^{j}\right] \delta(\gamma_{\text{azo}} - \alpha) \prod_{s} \left\{\delta\left[|\mathbf{u}_{\text{azo}}^{j}(s)| - 1\right]\delta\left[\mathbf{u}_{\text{azo}}^{j}(s) - \frac{1}{L}\frac{\mathrm{d}\mathbf{R}_{\text{azo}}^{j}(s)}{\mathrm{d}s}\right]\right\}$$

 $\quad \text{and} \quad$

$$Q_{\text{homo}}^{j}[\Omega] = \int \{ \mathcal{D}[\mathbf{R}_{\text{homo}}^{j}(s), \mathbf{u}_{\text{homo}}^{j}(s)] \exp\left\{-\beta \mathcal{H}_{0}[\mathbf{u}_{\text{homo}}^{j}(s)] - \int_{0}^{f_{\text{homo}}} \mathrm{d}s\omega \left[\mathbf{R}_{\text{homo}}^{j}(s)\right] \right\} \\ \times \delta\left[\mathbf{R}_{\text{homo}}^{j}(0) - \tilde{\mathbf{R}}_{\mathrm{I}}^{j}\right] \prod_{s} \left\{\delta\left[|\mathbf{u}_{\text{homo}}^{j}(s)| - 1\right] \delta\left[\mathbf{u}_{\text{homo}}^{j}(s) - \frac{1}{L} \frac{\mathrm{d}\mathbf{R}_{\text{homo}}^{j}(s)}{\mathrm{d}s}\right] \right\} (15)$$

respectively. The partition function of the nanoparticle is

$$Q_{\text{nano}}[\Omega, \eta_{\text{I}}] = \prod_{j=1}^{n_{\text{lig}}} \int \mathcal{D}[\mathbf{R}_{\text{lig}}^{j}(s), \mathbf{u}_{\text{lig}}^{j}(s)] \exp\left\{-\beta \mathcal{H}_{0}[\mathbf{u}_{\text{lig}}^{j}(s)]\right\}$$

$$\times \exp\left\{-\int_{0}^{f_{\text{lig}}} \mathrm{d}s\omega\left[\mathbf{R}_{\text{lig}}^{j}(s)\right] + \eta_{\text{I}}\left[\mathbf{R}_{\text{lig}}^{j}(f_{\text{lig}})\right]\right\}$$

$$\times \delta\left[\mathbf{R}_{\text{lig}}^{j}(0) - \tilde{\mathbf{R}}_{\text{II}}^{j}\right] \prod_{s} \left\{\delta\left[|\mathbf{u}_{\text{homo}}^{j}(s)| - 1\right]\delta\left[\mathbf{u}_{\text{lig}}^{j}(s) - \frac{1}{L}\frac{\mathrm{d}\mathbf{R}_{\text{lig}}^{j}(s)}{\mathrm{d}s}\right]\right\}.(16)$$

With the mean field approximation $\delta \mathcal{F}/\delta \Omega = \delta \mathcal{F}/\delta \eta_{I,II} = 0$, we have the self-consistent field equations

$$\omega(\mathbf{r}) = \kappa \rho(\mathbf{r}), \tag{17}$$

$$\eta_{\rm I}(\mathbf{r}) = -\tau \rho_{\rm azo, end}(\mathbf{r}), \tag{18}$$

$$\eta_{\rm II}(\mathbf{r}) = -\tau \rho_{\rm lig,end}(\mathbf{r}). \tag{19}$$

The force curve of nanoparticle



Figure S2: Force as a function of the center position of the nanoparticle under UV on and UV off conditions.

The force-distance curve is shown in Fig. S2, which can be measured by the single cell force spectroscopy. Initially, the force is positive around z = 1.0, which means that the nanoparticle suffers the repulsion from the grafted layer when it goes too close to the surface. When the nanoparticle is pulled from the surface, it suffers a restoring attractive force. Such attraction comes from the ligand-receptor interaction and the stretching of the polymer chains. The critical position is z = 1.1, beyond which the links of ligands and receptors begin to break down and the force starts to increase. When the nanoparticle completely leaves the surface, the force becomes zero. The valley of the force curve in the UV off state is much deeper than that in the UV on state.

Distribution of the receptors



Figure S3: Contour map of end-groups density distribution of azo-polymers under the UV off (left) and the UV on (right) conditions. Integral with respect to r coordinate gives rise to the end distribution show in Fig. 3(a) in the main text. These results show lateral inhomogeneous due to the adhesion of the nanoparticle.

Distribution of the azo-polymers



Figure S4: Contour map of total monomer density of the azo-polymers under the UV off (left) and the UV on (right) conditions. Here, f = 0.6 and $f_{\text{homo}} = 1.0$.

End distribution of the ligand polymers



Figure S5: Contour map of the ligand distribution under the UV off (left) and the UV on (right) conditions. The region below z = 1.0 is where the ligand-receptor interaction takes place.

Design of the surface according to the length of ligand polymer



Figure S6: Adhesion behavior for the nanoparticle with different lengths of the ligand polymer, f_{lig} , on the same hybrid surface under UV on conditions. Here, f = 0.6 and $f_{\text{homo}} = 1.0$.

It is very important to match the length of the ligand polymers with the length of the grafted polymers. Fig. S6 shows that the performance of the smart surface is quite poor when the length of ligand polymer is too long, because the ligand groups always have considerable probability to bond to the receptor groups.

Distribution of the azo-bonds of the conformations belonging to the Mode I and II



Figure S7: Distribution functions of the azo-groups of azo-polymers in different modes under the UV on condition.

The end distribution of the azo-polymers under the UV on condition can be decomposed into two modes, i.e., Mode I and Mode II. Mode I corresponds to the folding conformation and Mode II corresponds to the extending conformation. Although the end distribution functions of the two modes are quite different (shown in Fig. 5(b) and (c)), the azo-bond distributions almost coincide with each other.

Distribution of interaction region of double azo-bonds poly-

mer



Figure S8: Comparison of the distribution functions of ligand-receptor interaction of single azo-bond polymers with f = 0.3 (dotted line), f = 0.6 (dashed line), the double azo-bonds polymer (red line) under the UV on condition and that of the grafted layer under UV off condition (grey line). Introducing an extra azo-bond deforms the azo-polymer more compactly than that of single azo-bond condition and then the ligand-receptor interaction region greatly reduces.

References

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