Supporting information

Anisotropic exclusion effect between photocatalytic Ag/AgCl Janus particles and passive beads in a dense colloidal matrix

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Protocols and methods:

Substrate cleaning. Glass slides were used as a substrate. They were pretreated by immersion in a hot H_2SO_4/H_2O_2 (7 : 3) solution for 30 min followed by washing with a copious amount of deionized water.

Materials and Instruments. The PVP (Mw = 55000), Iron(III) chloride hexahydrate ($FeCl_3$•$6H_2O$), as well as polystyrene and SiO_2 particles (diameter of 2 μm) are from Sigma-Aldrich. The fluorescence lamp (HBO 103) is from Carl Zeiss Microscope. The light power detector and its monitor are from Genteceo.

Calculation of the exclusion area. The polygon area sub-routine from the data processing software Origin was used to calculate the exclusion area.

Video analysis. TrackMate from the image processing software Fiji (http://fji.sc/) was used to track trajectories of passive beads.

Numerical simulations: The behavior of a system consisting of active Janus particles and passive beads is simulated by numerically integrating the overdamped Langevin equations[35-36, 58-60]:

$$\begin{aligned} \dot{x}_i &= v_0 \cos\theta_i + \xi_{i0,x}(t) + \sum_{ij}^{N} f_{ij,x}, \\ \dot{y}_i &= v_0 \sin\theta_i + \xi_{i0,y}(t) + \sum_{ij}^{N} f_{ij,y}, \\ \dot{\theta}_i &= \xi_{i\theta}(t), \end{aligned} \qquad (1)$$

for *i, j* running from 1 to the total number *N* of particles, active and passive; v_0 is the self-velocity of Janus particles, which is set to zero for immobilized particles. Here, $\xi_{i0}(t) = (\xi_{i0,x}(t), \xi_{i0,y}(t))$ is a 2D thermal Gaussian noise with correlation functions $\langle \xi_{0,\alpha}(t) \rangle = 0$, $\langle \xi_{0,\alpha}(t)\xi_{0,\beta}(t) \rangle = 2D_T\delta_{\alpha\beta}\delta(t)$, where $\alpha, \beta = x, y,$ and D_T is the translational diffusion constant of a passive bead at fixed temperature; $\xi_\theta(t)$ is an independent 1D Gaussian noise with correlation functions $\langle \xi_\theta(t) \rangle = 0$ and

$\langle \xi_\theta(t)\xi_\theta(0)\rangle = 2D_R\delta(t)$ that models the fluctuations of the propulsion angle θ. The diffusion coefficients D_T and D_R can be directly calculated or extracted from the experimentally measured trajectories and MSD data, by fitting to the theoretical MSD.[36] Thus, for a particle with a diameter of 2 μm diffusing in water at room temperature, $D_T \approx 0.22$ μm^2/s and $D_R \approx 0.16$ rad^2/s.

The term, $\sum_{ij}^{N} f_{ij}$, represents, in a compact form, the sum of all inter-particle interaction forces in the system including[36]: (i) elastic soft-core repulsive interactions between passive beads and between active particles and passive beads and (ii) the effective repulsive interaction between Janus particles and passive beads due to the radial flow of products of chemical reaction from the surface of Ag/AgCl Janus particles illuminated by blue light. The latter contribution (ii) is modelled by a finite-range field of radial forces, decreasing in amplitude as $1/r$ from the centre of a Janus particle:

$$f_{ij}^{flow} = \begin{cases} \dfrac{\gamma(\theta)}{|\vec{r}_i - \vec{r}_j|}, & if\ |\vec{r}_i - \vec{r}_j| > R_i + R_j, \\ 0, & if\ |\vec{r}_i - \vec{r}_j| >> R_i + R_j, \end{cases} \qquad (2)$$

where $\gamma(\theta)$ is the cumulative "strength of the flow" parameter, which includes the flow of the fluid, the gradient of the concentration profile of the ions and other products of the chemical reaction from the surface of the AgCl particle illuminated by blue light. For the asymmetric flow distribution, the parameter $\gamma(\theta)$ is not a constant but essentially an angle-dependent function. We assume that the maximum flow strength is in the direction away from the cap and it decreases with the distance from the cap. This decrease is modeled by the expression consisting of symmetric and anisotropic parts, as clarified in the main text. From the calibration of the simulated trajectories and the MSD of beads to the experimentally measured MSD, we found[36] that for a single Janus

particle $\gamma \approx (3.2 - 3.9)$ $\mu m^2/s$. In the calculations carried out in this work, the value $\gamma = 3.5$ $\mu m^2/s$ is used as the maximum value of the flow strength.

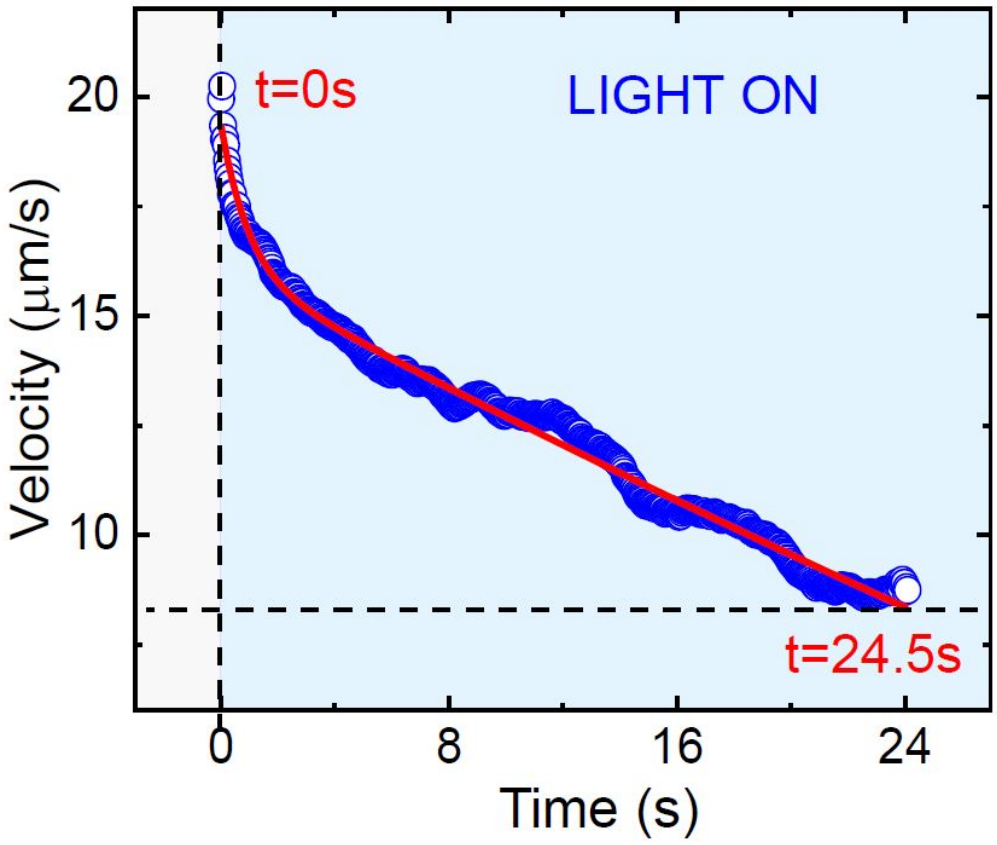
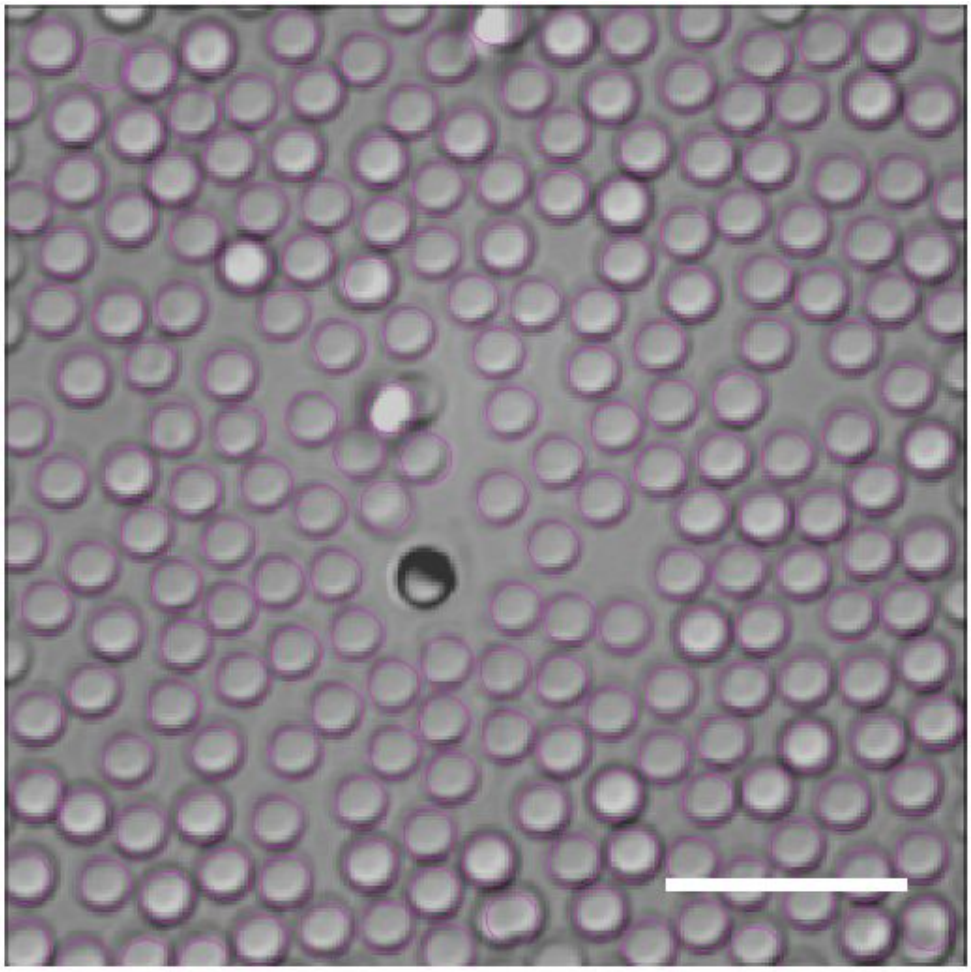


Figure S1. Experimental data showing the change of the velocity of a Ag/AgCl Janus micromotor, which is propelling due to the photocatalytic reaction upon illumination with blue light (wavelength of 450 nm - 470 nm; intensity of 137 µW/mm^2). Red solid line is a fit to the experimental data.



Zone	t = 0 s
Number of particles	215
Area (μm^2)	1421.29
Density (particles/μm^2)	0.151

Figure S2. A snapshot of the Video S1 showing a distribution of passive beads around a Janus particle (the one with a black cap). The image is taken under illumination with a reference white light before the blue light is turned on. This image is used to calculate

the area density of passive beads. Beads indicated with circles are included in the calculation. Scale bar, 10 μm.

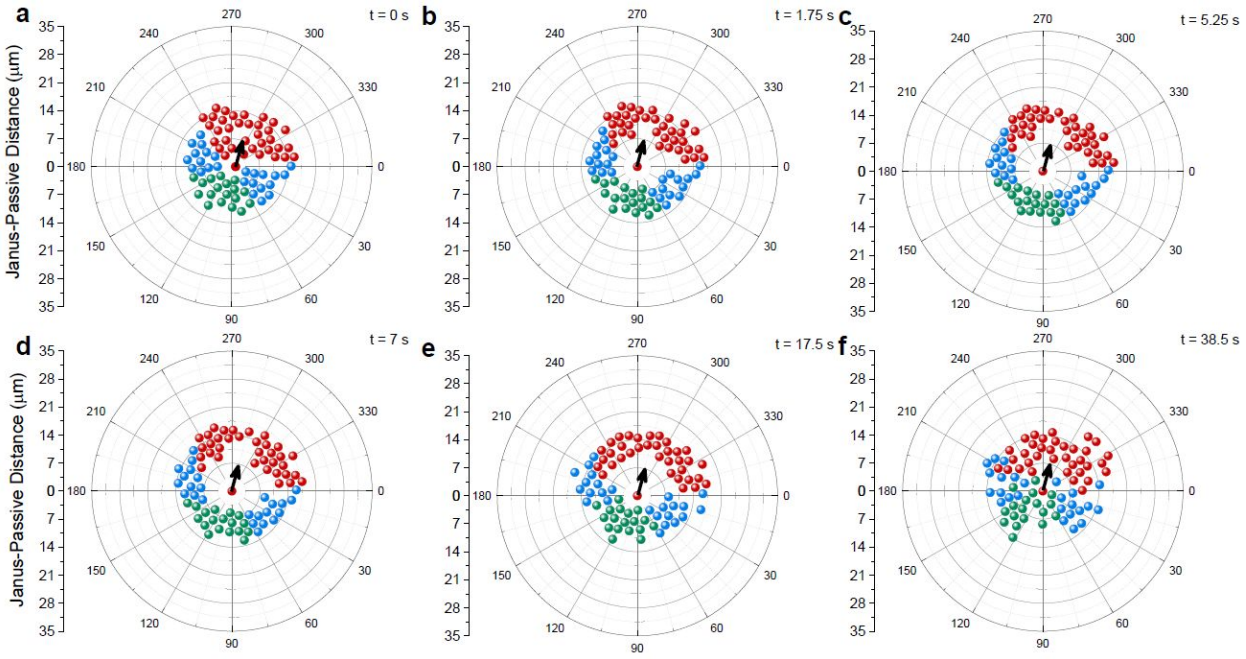


Figure S3. Experimental study of the interaction process in a system containing an immobile Janus particle and passive beads under blue light illumination. (a-f) Time evolution of the distance between a Janus particle and passive beads. The Janus particle is located in the center of the graph and the orientation of its cap is shown with a black arrow. Passive beads are assigned to different groups accounting for their position with respect to the cap of the Janus particle. The color coding is as in Figure 1d of the main text: in red (in front of the cap of the Janus particle), in green (behind the Janus particle facing its PS side) and in blue (from both sides of the Janus particle).

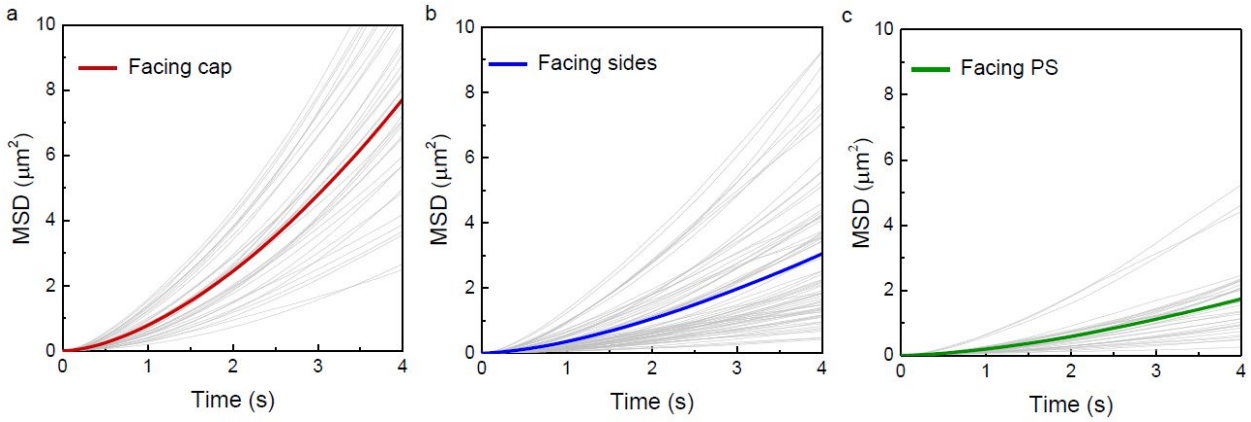
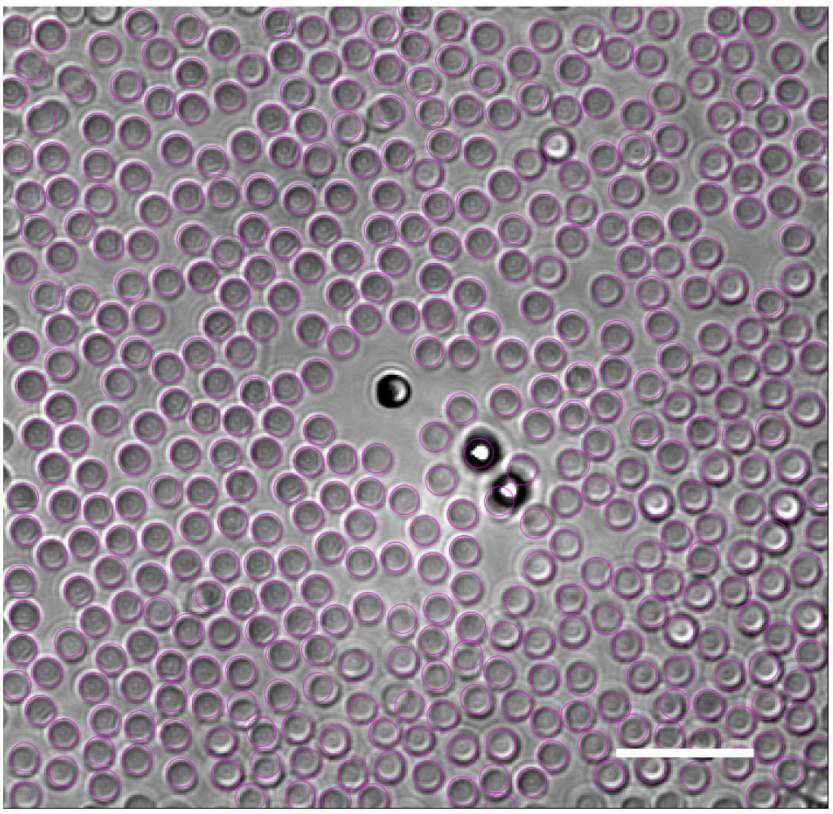


Figure S4. Theoretical study of the interaction process in a system containing an immobile Janus particle and passive beads. (a-c) MSD curves for all tracked passive beads (gray lines). The corresponding trajectories are show in Figure 3b of the main text. The MSD curves shown with red (a), blue (b) and green (c) are the result of averaging over all MSD curves shown in the respective panels. The color coding is as in Figure 1d of the main text: in red (in front of the cap of the Janus particle), in green (behind the Janus particle facing its PS side) and in blue (from both sides of the Janus particle).



Zone	t = 0 s
Number of particles	433
Area (μm²)	3171.25
Density (particles/μm²)	0.136

Figure S5. A snapshot of the Video S2 showing a distribution of passive beads around a Janus particle (the one with a black cap). The image is taken under illumination with a reference white light before the blue light is turned on. This image is used to calculate the area density of passive beads. Beads indicated with circles are included in the calculation. Scale bar, 10 μm.

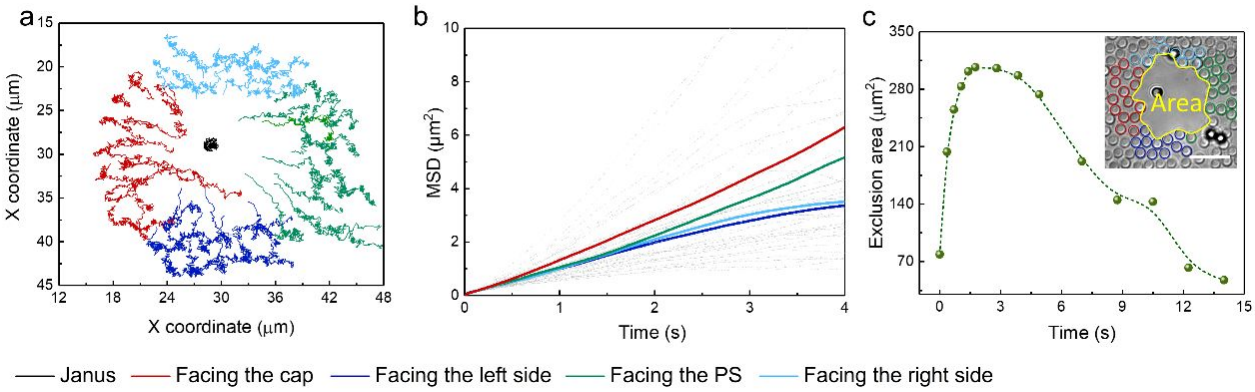


Figure S6. Experimental study of the interaction process in a system containing passive beads and a Janus particle, which can perform rotational but no translational motion, under blue light illumination (wavelength of 450 nm - 470 nm; intensity of 137 μW/mm^2). (a) Trajectories of passive beads are color coded in four groups accounting for their position with respect to the cap of the Janus particle (the color scheme is the same as in Figure 4a of the main text): in red (in front of the cap of the Janus particle), in green (behind the Janus particle facing its PS side), in blue (on the left side of the Janus particle) and in light blue (on the right side of the Janus particle). (b) The corresponding MSD curves for all tracked passive beads (gray lines). The MSD curves shown with red, blue, green and light blue color are the result of averaging over all MSD curves taken of the beads belonging to one of the four groups. (c) The time evolution of the exclusion area. The insert demonstrates one of the snapshots of the Video S2 (illumination for 3.5 s), with the exclusion area indicated with a yellow line. Scale bar, 10 μm.

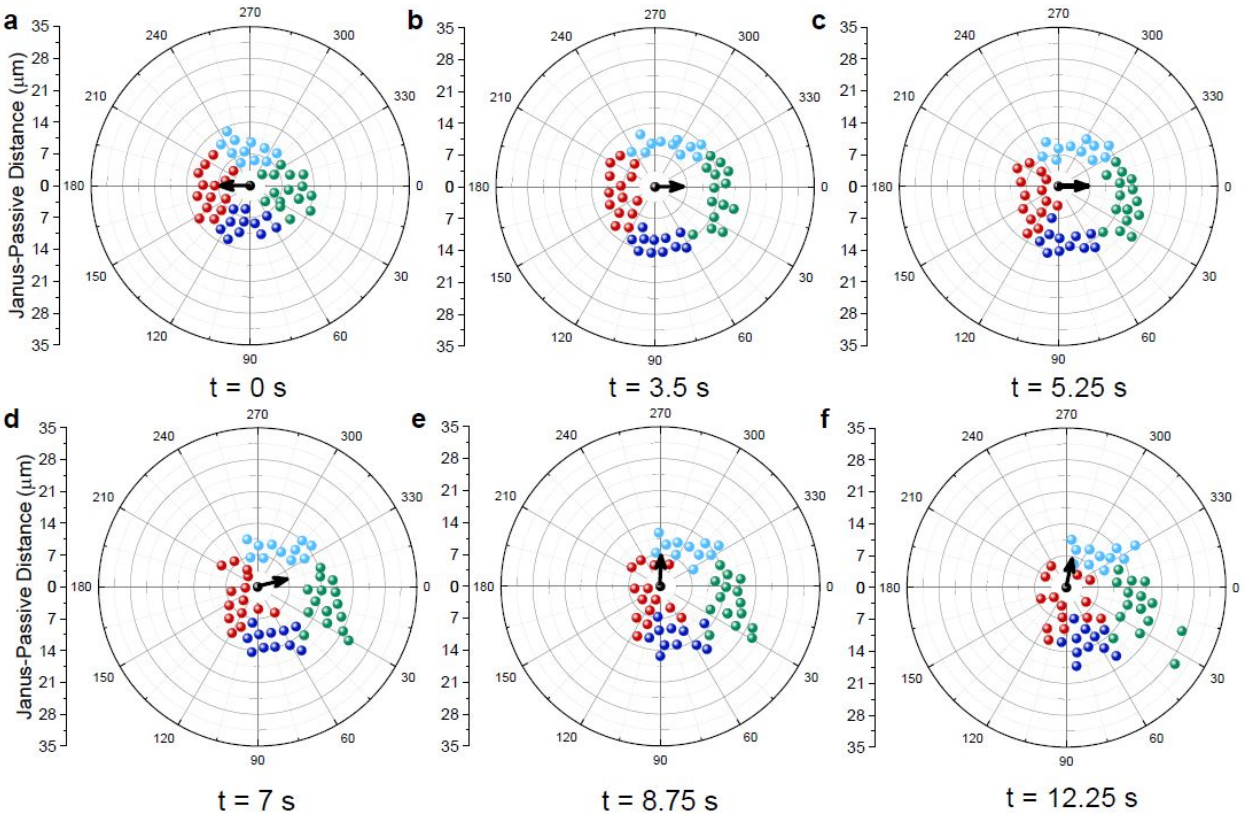


Figure S7. Experimental study of the interaction process in a system containing passive beads and a Janus particle, which can perform rotational but no translational motion, under blue light illumination (wavelength of 450 nm - 470 nm; intensity of 137 µW/mm^2). (a-f) Time evolution of the distance between a Janus particle and passive beads. The Janus particle is located in the center of the graph and the orientation of its cap is shown with a black arrow. Passive beads are assigned to different groups accounting for their position with respect to the cap of the Janus particle. The color coding is as in Figure 4a of the main text: in red (in front of the cap of the Janus particle), in blue (at the left side of the Janus particle), in

green (behind the Janus particle facing its PS side) and in blue (at the right side of the Janus particle).

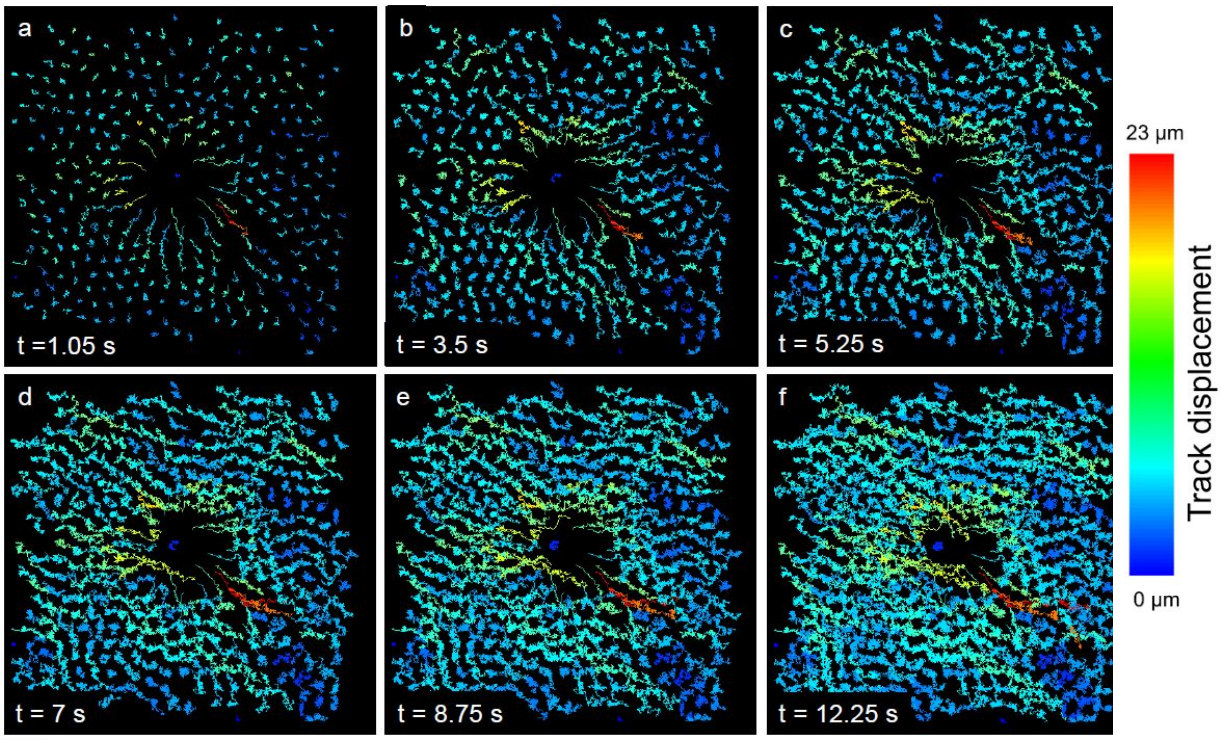


Figure S8. Experimental study of the interaction process in a system containing passive beads and a Janus particle, which can perform rotational but no translational motion, under blue light illumination. (a-f) A series of snapshots of the Video S2 showing the time evolution of the displacement of passive beads and a Janus particle upon illumination with blue light (wavelength of 450 nm - 470 nm; intensity of 137 µW/mm^2). The traveled distances of each interacting object are color coded with respect to their length (small displacement – blue, large displacement – red). Scale bar, 10 µm.