Manipulation of optical microcavities using a magnetic field is a novel and clean strategy as the molecular structure and its packing are not affected in this technique, unlike in mechanical and light-based ones. As a proof of principle, herein magnetic field–triggered orientation of polystyrene optical cavities loaded with 1) red-emitting dye and 2) magnetic iron oxide nanoparticles is demonstrated. Due to the incorporation of the dye, the nonemissive polymer cavities show whispering gallery modes in the fluorescence spectra with the Q-factor in the range of 400. Further, the integration of iron oxide nanoparticles facilitates the collective alignment of polymer cavities efficiently depending upon the applied magnetic field direction. The presented new method, which combines magnetic field–assisted micromanipulation and organic nanophotonics, is anticipated to offer prospects in the area of biophotonics, biomedicine, and magnetic field sensors.

1. Introduction

Stimuli-responsive nano/microoptical entities, viz., waveguides,[31] cavities,[2] modulators,[33] and lasers,[8] are crucial for the advancement of next-generation nanophotonic materials. Molecular or polymer optical materials responding to external stimuli, viz., light,[1,5] mechanical force,[6] temperature,[54] and chemicals,[53] are very well studied in the literature. In most of the stimuli experiments involving photonic objects, the response was 1) demonstrated at single-particle level and 2) triggered by a change in the molecular structure/packing in the solid state.[1–7] Attaining collective macroscopic response from photonic objects is essential to create reconfigurable laser arrays and coupled-resonator optical waveguides in addition to studying the magneto-optical effects. The magnetic field is an ideal trigger to obtain a collective macroscopic response from the objects without making any physical contacts. Further, the response to the magnetic field arises without affecting the molecular structure and its internal solid-state packing within the object. Realization of the idea of magnetic field–induced collective microscopic response from optical entities requires the incorporation of nanomagnets or magnetic nanoparticles (NPs) within them, and this notion was not tested in the literature until this report. We envisioned magnetic manipulation of polymer optical cavities made by integrating magnetic iron oxide NPs and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylamino styryl)-4-H-pyran (DCM) dye within polystyrene (PS) microparticles.

Magnetic iron oxide NPs (Fe NPs), for example, magnetite (Fe₃O₄) and/or maghemite (γ-Fe₂O₃), are ideal candidates for this experiment because of their high saturation magnetization, good biocompatibility, chemical stability, and magnetoelectric properties.[8] The small size of Fe NPs facilitates their easy integration into the polymer matrix. Further, the magnetic moment of each Fe NP embedded within the polymer can be made ordered with respect to the external magnetic field direction. PS is one of the well-known materials for creating optical cavities via self-assembly technique.[23–16] PS provides a fairly high refractive index (n) and therefore acts as an effective gain medium providing optical cavities with a high quality factor (Q-factor), which is proportional to the decay time of light. The formation of spherical particles from dye-doped PS enables trapping of the dye fluorescence (FL). The repeated circulation of trapped photons via repeated total internal reflection facilitates the emission of whispering-gallery-mode (WGM) radiation[14] with the Q-factor in the range of several hundreds. The realization of cavities of different diameters also provides control over the number of emitted optical modes.

Here, for the first time, we report optical microcavities that are responsive to magnetic stimuli. These cavities were realized by utilizing PS as a gain medium, DCM dye as an active medium,
and Fe NPs as a trigger for magnetic manipulation of optical cavities (Scheme 1A). Single-particle optical studies revealed the WGM radiation from the cavities with a $Q$-factor around 400. Judicial incorporation of Fe NPs into the polymer microcavities did not affect the cavity property. In the presence of an applied external magnetic field, the Fe–DCM–PS microcavities self-organize themselves to form anisotropically aligned cluster chains in the direction of the magnetic field (Scheme 1B,C).

2. Results and Discussion

2.1. Self-Assembly of Polymer Optical Microcavities Loaded with Fe NPs

The preparation technique of Fe NPs and DCM dye loaded PS microparticles is given in Scheme 1A. The Fe-NPs were prepared as per the reported procedure. Analysis of the powder X-ray diffraction (PXRD) peaks of the Fe NPs indicated that the obtained NPs were mostly of $\gamma$-Fe$_2$O$_3$, with some Fe$_3$O$_4$ (Figure 1A). The as-prepared NPs also showed magnetic field–induced alignment in the bulk state. Fe–DCM–PS microcavities were prepared by a self-assembly method using PS, DCM dye, and Fe NPs in a tetrahydrofuran (THF)/water mixture. The mixture (50 μL) was drop casted on to a clean coverslip and underwent solvent evaporation at ambient condition. Observation of the formed microparticles under a confocal microscope showed circular structures, confirming the formation of microspheres. These particles were used for morphological, optical, and magnetic field–induced manipulation studies.

2.2. Optical and Morphological Studies of Fe–DCM–PS Microspheres

The optical absorbance spectra of Fe–DCM–PS particles dispersed in ethanol exhibited absorbance maximum at 465 nm akin to DCM–PS particles (Figure 1B). However, the former absorbance spectrum showed a weak and broadband peak from ~525 to 750 nm due to the presence of Fe-NPs. Both...
Fe–DCM–PS and DCM–PS particles displayed red FL of DCM dye with a band maximum centered at 592 nm (Figure 1B). The morphology of Fe–DCM–PS microparticles was examined under a laser confocal optical microscope (LCOM) and field-emission scanning electron microscopy (FESEM). LCOM images revealed the circular shape of the particles of various sizes. The polydisperse nature of the microparticles is also vital for comparative size-dependent photonic studies down to single-particle level. The spherical geometry of the Fe–DCM–PS microparticles was confirmed by top- and side-view field emission scanning electron microscopy (Figure 2B,C). The smooth surface of the spherical microparticle is crucial for it to act as a high-Q optical cavity, due to the minimization of scattering-induced optical loss. The amount of Fe NPs incorporated into the PS microparticle plays a vital role in adjusting the surface smoothness of the microcavity. Small crater-like features were found on the surface of the Fe–DCM–PS microparticles compared to that of pure DCM–PS microspheres (Figure 2D). The close view of the microparticles clearly shows the crater-like deformations are only on the surface of the microspheres, which could be possibly formed due to the attachment of water droplets during the growth of microparticles. Earlier, we observed similar features in PS particles when doped with perovskite NPs.[22] The chemical composition of these microspheres was further confirmed by energy-dispersive X-ray analysis (EDAX) (Figure 2 E,F). The EDAX spectrum denotes the presence of elements such as C, N, O, and Fe. This result further confirms the incorporation of DCM and Fe NPs within the spherical polymer microparticles.

### 2.3. Single-Particle Microspectroscopy Studies of Fe–DCM–PS Microspheres

The photonic cavity properties of obtained Fe–DCM–PS microspheres were evaluated using an LCOM. Excitation of a single Fe–DCM–PS microsphere with a continuous wave laser (405 or 488 nm) displayed a red FL. The FL spectrum also showed a series of pairs of sharp peaks (Figure 3A). These peaks arise as a result of the confinement of repeatedly circulating FL photons (via total internal reflection at the air–particle interface) within the spherical microparticle. This FL confinement creates optical interference and subsequent WGMs. Each pair of peaks corresponds to transverse magnetic (TM) and transverse electric (TE) fields. In TE modes, the electric field of the electromagnetic radiation is parallel to the surface of the microcavity. In contrast, in TM modes, it is the magnetic field of the electromagnetic radiation, which is parallel to the microcavity surface. The FL spectra of DCM–PS and Fe–DCM–PS resembled each other without any changes in the spectral feature, which confirms the noninterference of magnetic NPs in the cavity properties (Figure 3B).

The spacing between successive optical modes (Δλ), i.e., the free spectral range (FSR), and the Q-factor were calculated for microcavities of different sizes. As displayed in Figure 4A, the three representative microcavities with different sizes were excited with a 405 nm (0.1 mW) laser to collect the FL spectrum with WGM signature. Comparison of the spectra of the cavities showed an increase of FSR values upon decreasing cavity diameter (D). The experimentally determined FSR values of cavities with D of 5.6, 4.2, and 3.0 μm were 17.3, 23.6, and 30.9 nm, respectively (Figure 4A). This observation is in line with the equation $\text{FSR} = \frac{\lambda^2}{\pi D n_{\text{eff}}}$, where $\lambda$ is the wavelength of light and $n_{\text{eff}}$ is the effective refractive index (Figure 4C). A 3D finite difference time domain (FDTD) numerical method was used to calculate the azimuthal number of the modes (for radial mode number, $r = 1$; for polar and azimuthal mode number, $l = m$) and the corresponding electric field distributions of selected optical modes in the microcavities (Figure 4B). The calculated $m$-numbers (TE and TM) of a pair of peaks of cavities with $D$ of

![Figure 2. A) Confocal microscopic image and B,C) FESEM images of Fe–DCM–PS microspheres. D–F) Energy-dispersive elemental mapping of a single microsphere and percentage of elemental distribution.](image-url)
5.6, 4.2, and 3.0 μm are given in Figure 4A. The calculated data of cavities with D of 5.6, 4.2, and 3.0 μm show the distribution of the electric fields of TM_{17}, TM_{24}, and TM_{34} modes located at the circumference of the microcavities. The Q-factor of the microcavities increased with their diameter. The measured Q-factors of the microcavities are around 400 (λ = 610 nm, full width at half-maximum = 1.4 nm) (Figure 4D).

Further, as the concentration of Fe NPs in DCM–PS microspheres was kept low to create defect-less optical cavities, the magnetic field–induced variation of the refractive index of the material was too small for the observation of magnetization-induced modulation of the resonant properties of the microcavities.

2.4. Alignment of Fe–DCM–PS Optical Cavities Under an External Magnetic Field

Self-assembly of Fe–DCM–PS optical cavities in the absence of a magnetic field showed isotropic distribution without any
orientation preference. Although the individual Fe NPs have ordered magnetic moments, in the absence of a magnetic field, the net magnetic moment is zero; as a result, it leads to an isotropic distribution of Fe–DCM–PS cavities. The magnetic alignment of Fe–DCM–PS optical microcavities was envisaged by drop casting the sample in the presence of a bar magnet with a magnetic field of ≈200 G. This was accomplished by keeping a bar magnet below the coverslip before the sample deposition (Scheme 1C). The presence of the magnetic field ensured the orientation of microcavities as cluster chains aligning with the magnetic flux direction (Figure 5A–C). The alignment was intact even after removal of the external magnetic field. The alignment of microcavities is a result of the net statistical alignment of individual Fe NPs within each microcavity. In each cluster, the number of microcavities varied. Also, the directional dependence of microcavities was further confirmed as their orientation changed during self-assembly when the magnet was rotated by 90° (Figure 5E–G). The FESEM images of the cluster chains of microcavities exhibited the presence of microcavities of various sizes in each cluster (Figure 5D,H). Optical experiments performed on the microcavity of a cluster chain also exhibited WGMs.

3. Conclusion

In summary, for the first time, we prepared magnetic iron-NP-loaded polymer optical microcavities, which can be oriented by applying an external magnetic field. For the preparation of the microcavities, a three-in-one strategy was followed by incorporating 1) magnetic Fe NPs, 2) red DCM dye as an active medium, and 3) PS as a gain medium. The resultant cavities showed size-dependent optical WGMs in the FL spectra due to the recurrent circulation of FL photons via total internal reflection at the cavity and air boundary. The microcavities also revealed characteristic TE and TM modes from the WGM cavities. The FDTD calculations confirmed the radial mode number \( r = 1 \), and equal polar and azimuthal mode numbers \( l = m \). The calculation also demonstrated the distribution of the electric field of the optical modes around the spherical particle boundary. The Q-factor of the microcavities was as high as 400. Self-assembly of microcavities in the presence of a magnetic field resulted in their alignment due to the incorporation of magnetic Fe NPs.

4. Experimental Section

**Preparation of Fe–DCM–PS Microparticles:** PS (2.5 mg) beads were dissolved in THF (4 mL) followed by addition of DCM dye (1 mg). To this mixture Fe NPs (1 mg) dispersed in THF (2 mL) were added. The mixture was sonicated for 5 min to obtain homogeneous distribution, and then 1 mL of water was rapidly injected. The mixture was left undisturbed for about 10 min to facilitate the formation of microparticles.

**Electron Microscopy Studies:** The morphology of the prepared Fe–DCM–PS microcavities were examined under a 3 kV Zeiss FESEM.

**Confocal Microspectroscopy:** Single-particle microspectroscopy experiments were performed in a transmission mode setup of the Wi-Tec alpha 300 AR LCOM equipped with a Peltier-cooled CCD detector. Using a 300 grooves mm\(^{-1}\) grating blazed at 750 nm, the accumulation time was 5 s and the integration time was typically 1.0 s. Ten accumulations were averaged for a single spectrum. A 488 nm Ar\(^+\) continuous wave laser was used as the excitation source for the optical studies of microparticles. A 20× objective was used for collection of images, and 150× for collection of the FL spectrum.

**FDTD Calculations:** The calculations were made using Lumerical FDTD Solutions. The simulations were performed in 2D, and geometrical parameters of microresonators were retrieved from optical images; for the simulations a point dipole source with a wavelength range corresponding to emission inside the resonator was used. The refractive index was taken to be 1.55.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

magneto-optical cavities, mechanophotonics, optical cavities, whispering gallery modes
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