Photochemical evaluation of dual fluorescence of a novel DNA groove binder

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ABSTRACT

We synthesized the fluorophore-tethered oligopeptide showing a dual fluorescence in water, and the ratiometric fluorescence change of the modified oligopeptide was induced by the binding to DNA. The equilibrium of the modified oligopeptide between two excited states, a locally excited (LE) state and an intramolecular charge transfer (ICT) state, was controlled depending on DNA structures.

RESULTS AND DISCUSSION

The synthesis of the fluorophore-tethered oligopeptide was outlined in Scheme 1. An oxadiazole derivative 2, which was prepared in four steps according to the previous report, was coupled with monobrominated formyl triphenylamine 1 via Heck reaction to give 3. The fluorophore was incorporated into an oligopeptide through the reductive amination of the formyl group of the fluorophore with the N-terminus of the oligopeptide on solid supports. After cleavage from the resin, the modified oligopeptide was purified through denaturing SDS polyacrylamide gel, and identified with MALDI-TOF mass spectrometry.

The two fluorescence bands at 495 and 365 nm were assigned to the ICT and LE fluorescence bands, respectively, by investigating the photophysical behavior of the fluorophore. Only one broad emission band at 495 nm was observed for 1 in water on excitation at 360 nm. This emission band showed a strong solvatochromicity, which can be assigned to ICT fluorescence, and shifted to longer wavelength in highly polar solvents (450 → 495 nm). From the solvatochromic plot of these data for the wavenumbers
CONCLUSION

In conclusion, we synthesized a fluorophore-tethered oligopeptide showing a dual fluorescence behavior in water, and the equilibrium between LE state and ICT state was controlled by the addition of DNA.

REFERENCES

