

Supporting information

Synthesis of the DNA-[Ru(tpy)(dppz)(CH₃CN)]²⁺ Conjugates and their Photo Cross-Linking Studies with the Complementary DNA Strand

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Legends for Figures S1 – S6.

- Figure S1:** Reversed-phase HPLC purification of (A) ODN **II** containing amino-linker **L** at the 3'-terminal of oligo sequence; (B) preparative HPLC after the reaction of pure ODN **II** and **7** overnight at room temperature to give ODN **VIa** + **VIb**. Fractions **VIa** and **VIb** correspond to the mixtures of diastereomers for the 3'-[Ru(tpy)(dppz)(NCCH₃)²⁺]-ODN conjugate. (C) Analytical co-injection of the purified diastereomers of the 3'-[Ru(tpy)(dppz)(NCCH₃)²⁺]-ODN **VIa** + **VIb**. Eluent: 0.1 M Et₃NH⁺AcO⁻ with linear gradient of 0 – 30% MeCN in 80 min, followed by 30 – 50% MeCN in 10 min (see Experimental Part for details).
- Figure S2:** UV-vis absorption spectra (A) and (B) of aqueous solution of fractions [see Fig S1 (C)] eluting (R_t) at 52.7 min [Fraction **VIa**] and at 54.4 min [Fraction **VIb**], respectively, which were isolated in the course of HPLC purification of the reaction mixture containing ODN **II** and **7**. (C) UV-vis absorption spectra of compound [Ru(tpy)(dppz-L)(CH₃CN)](PF₆)₂ **17**, where **L** is a linker, CONH(CH₂CH₂O)₂CH₂CH(OH)CH₂OH (see Scheme 2 for synthesis) for comparison with the fractions **VIa** and **VIb**. (see Experimental Part for details).

3. **Figure S3:** UV-vis absorption spectra of $[\text{Ru}(\text{tpy})(\text{dppz-L})(\text{X})](\text{PF}_6)_2$ in acetonitrile solution, where **L** is a linker, $-\text{CONH}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, and $\text{X} = \text{Cl}^-$ (compound **13**, solid line), or acetonitrile (compound **17**, dotted line), or pyridine (compound **16**, dashed line). Ru^{2+} complexes **13**, **16** and **17** have been synthesized according to Scheme 2 (see Experimental Part for details).
4. **Figure S4:** Reversed-phase HPLC purification of ODNs **I**, **III**, and **IV** (A - C) containing amino-linker **L** at the 5'-end, at the middle, and at both 3'- and 5'-ends of oligo sequence; (D - F) preparative HPLC profiles after the reactions of the pure ODNs **I**, **III**, or **IV** with the Ru^{2+} complex **7** overnight at room temperature ($\text{I} + \mathbf{7} \rightarrow \text{V}$, $\text{III} + \mathbf{7} \rightarrow \text{VII}$, $\text{IV} + \mathbf{7} \rightarrow \text{VIII}$). Two fractions **Va** and **Vb** correspond to the mixtures of diastereomers for the 5'- $[\text{Ru}(\text{tpy})(\text{dppz})(\text{NCCH}_3)^{2+}\text{-ODN}$ conjugate **V**. The corresponding fractions for conjugates **VII** and **VIII** were poorly resolved and, hence, were not separated. Eluent: 0.1 M $\text{Et}_3\text{NH}^+\text{AcO}^-$ with linear gradient of 0 - 30% MeCN in 80 min, followed by 30 - 50% MeCN in 10 min (see Experimental Part for details). Yields are shown in Table 1.
5. **Figure S5:** ESI (A) and MALDI-TOF (B) mass spectra of the 3'- $[\text{Ru}(\text{tpy})(\text{dppz})(\text{CH}_3\text{CN})]^{2+}\text{-ODN}$ conjugate **VIa**. ESI data shown is a deconvoluted spectra constructed from m/z data for several charge states. Formulas of 1- charged ions corresponding to the main peaks are shown on the top of each MS spectra. The peak with m/z 4039.8 corresponds to the $\text{Ru}^{2+}\text{-ODN}$ conjugate with matrix molecule (2,4,6-trihydroxyacetophenone, MW = 168) bound instead of the substituted CH_3CN .
6. **Figure S6:** (A - C) aqueous solutions of ODNs **V** - **VII** before (straight line) and after (broken line) irradiation for 1 h. Concentrations of ODN and non-tethered complexes were adjusted to $5.5 \times 10^{-6} \text{ mol l}^{-1}$.

Figure S1

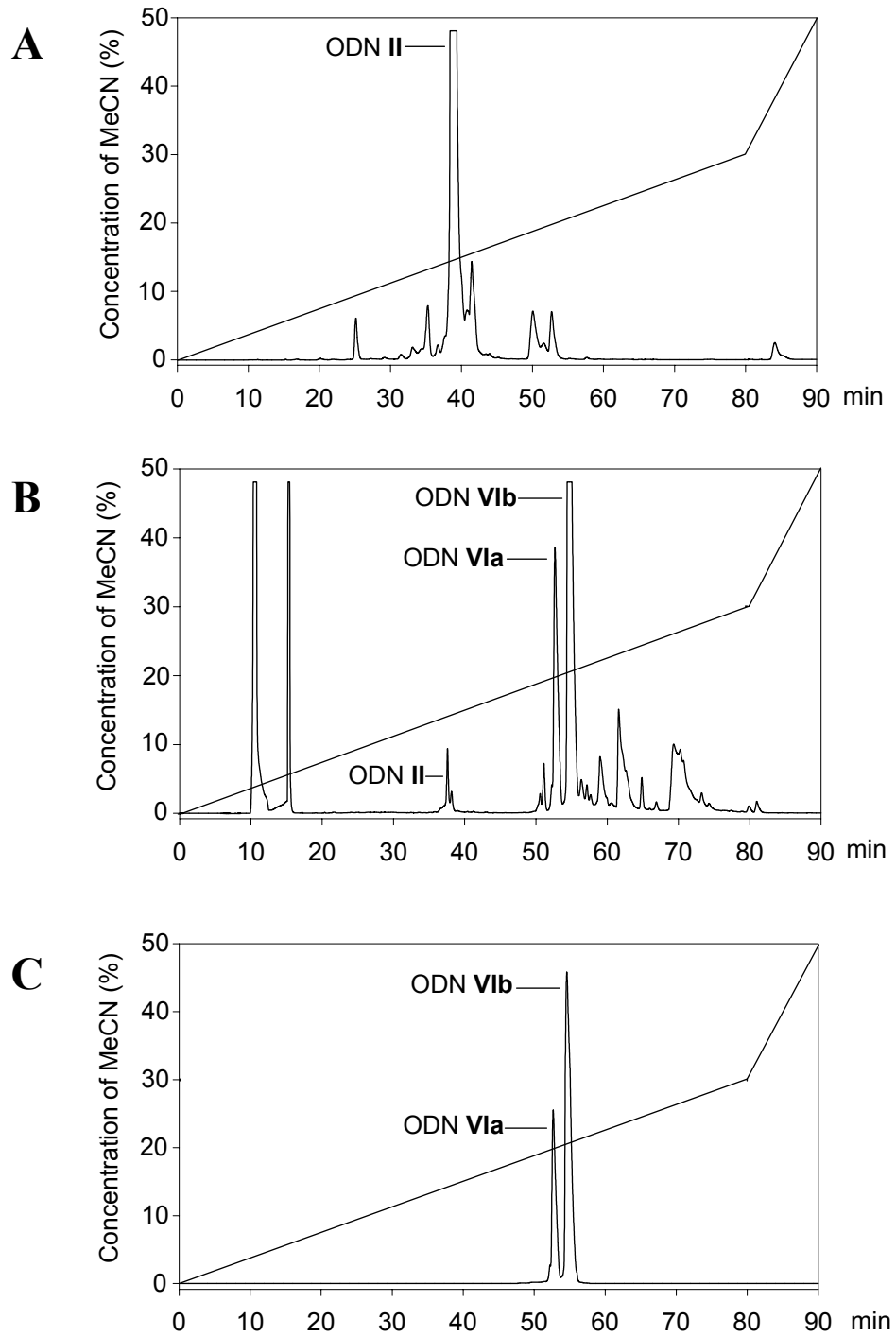


Figure S2

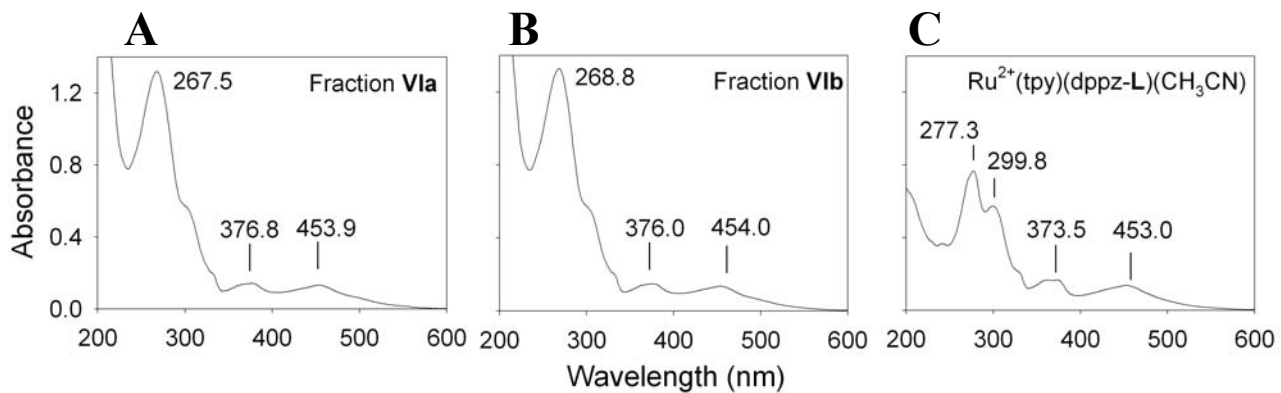


Figure S3

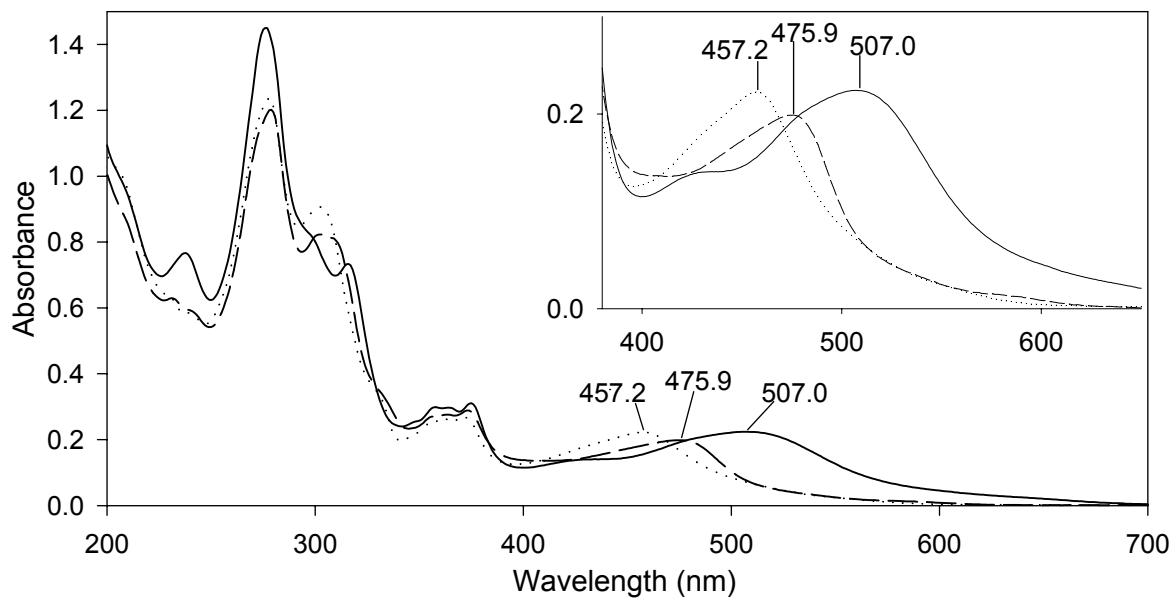


Figure S4

