Supplementary Information (SI) for Physical Chemistry Chemical Physics.
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Supplementary Material: Modeling Infrared and Vibrational Circular Dichroism Spectra of Complex Systems: the DFTB/Fluctuating Charges Route

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S1 DNA and DOX/DNA in aqueous solution

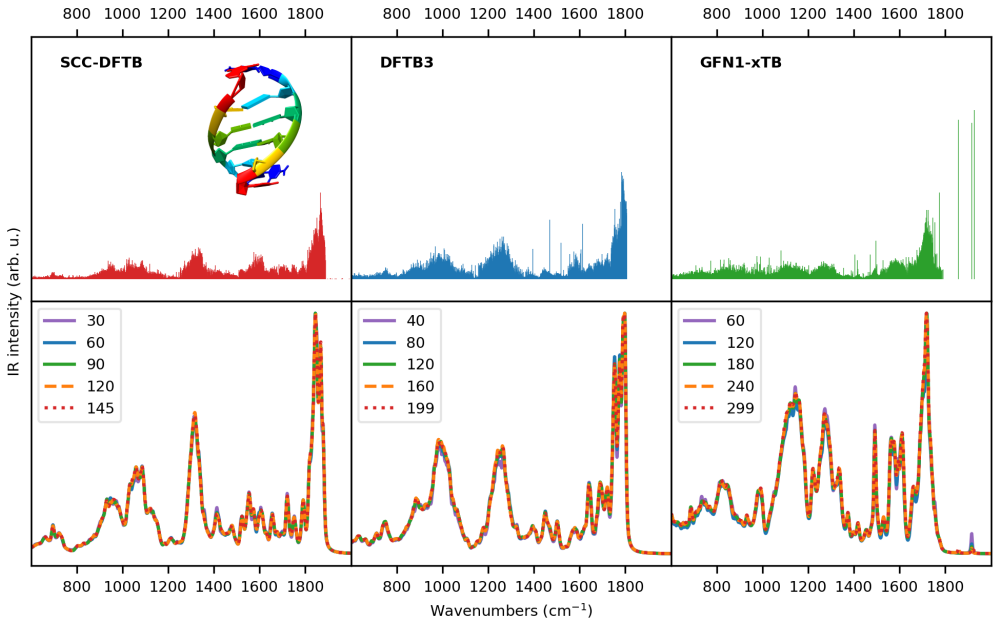

Figure S1: IR stick spectra (upper panel) and convergence analysis (lower panel) for aqueous DNA as obtained with diverse DFTB/FQ methods.

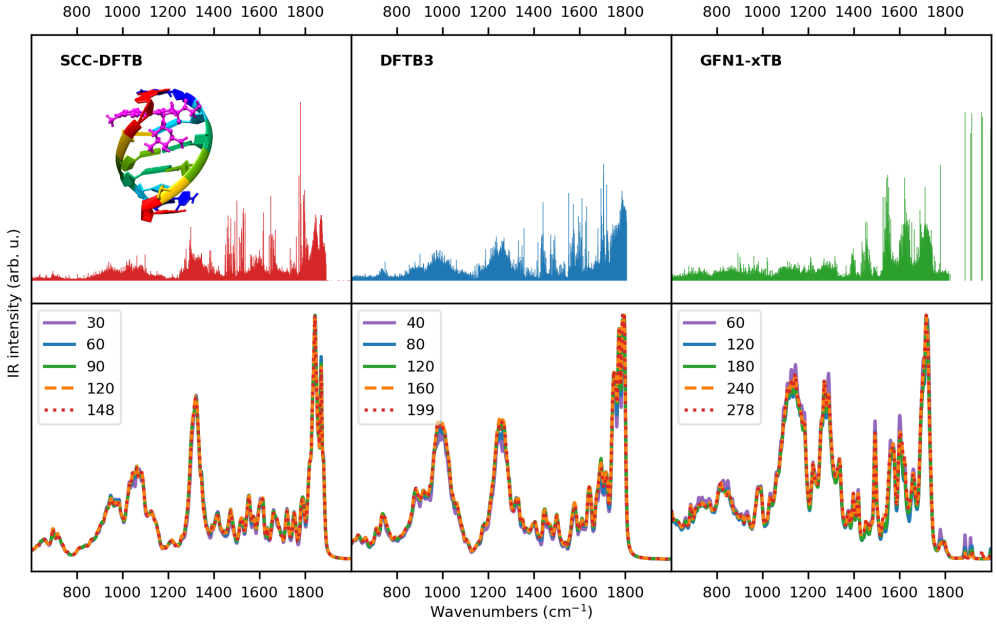

Figure S2: IR stick spectra (upper panel) and convergence analysis (lower panel) for aqueous DOX/DNA as obtained with diverse DFTB/FQ methods.

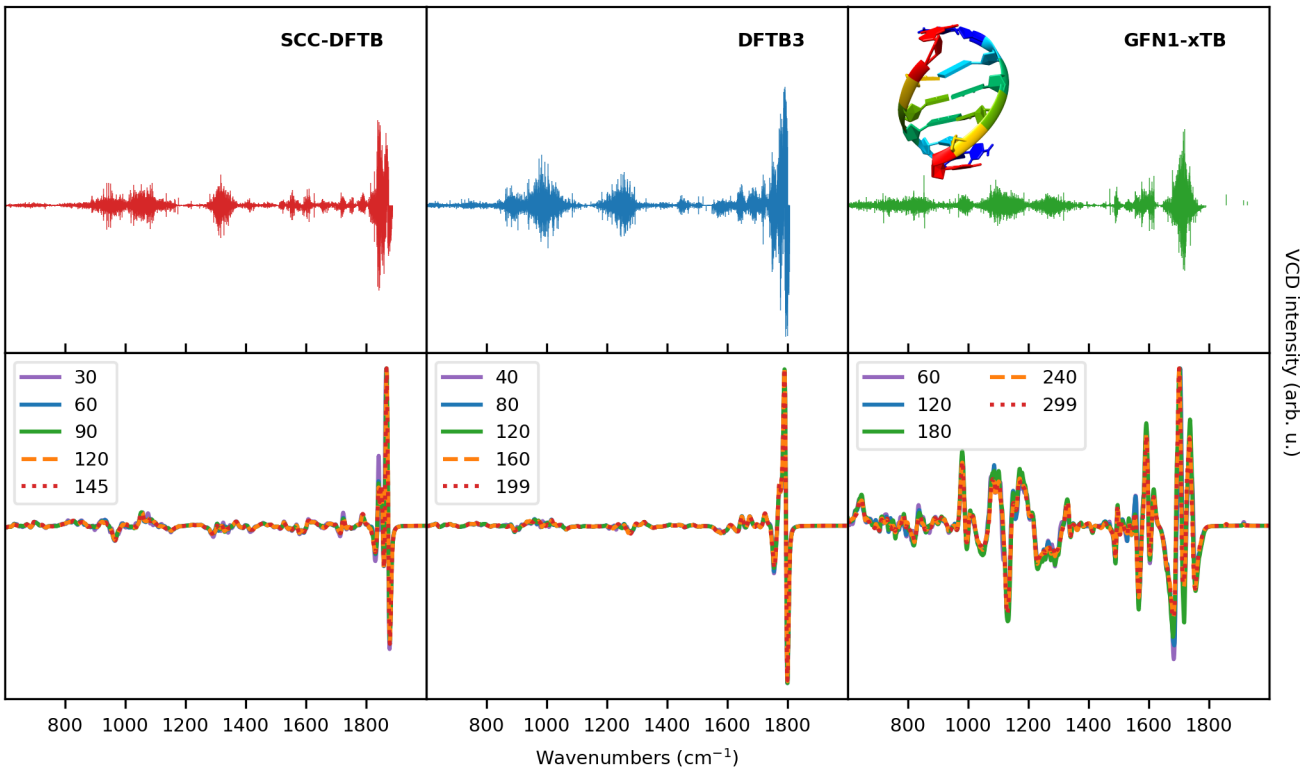

Figure S3: VCD stick spectra (upper panel) and convergence analysis (lower panel) for aqueous DNA as obtained with diverse DFTB/FQ methods.

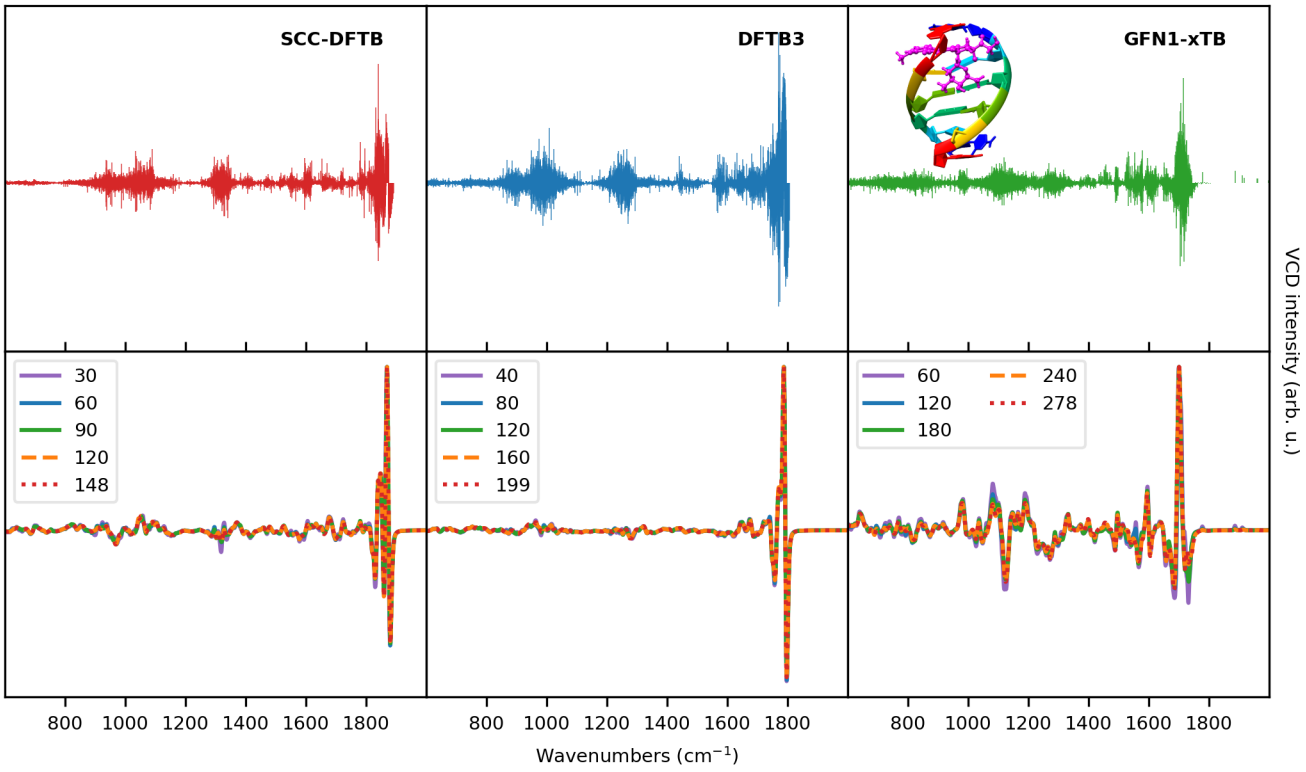

Figure S4: VCD stick spectra (upper panel) and convergence analysis (lower panel) for aqueous DOX/DNA as obtained with diverse DFTB/FQ methods.

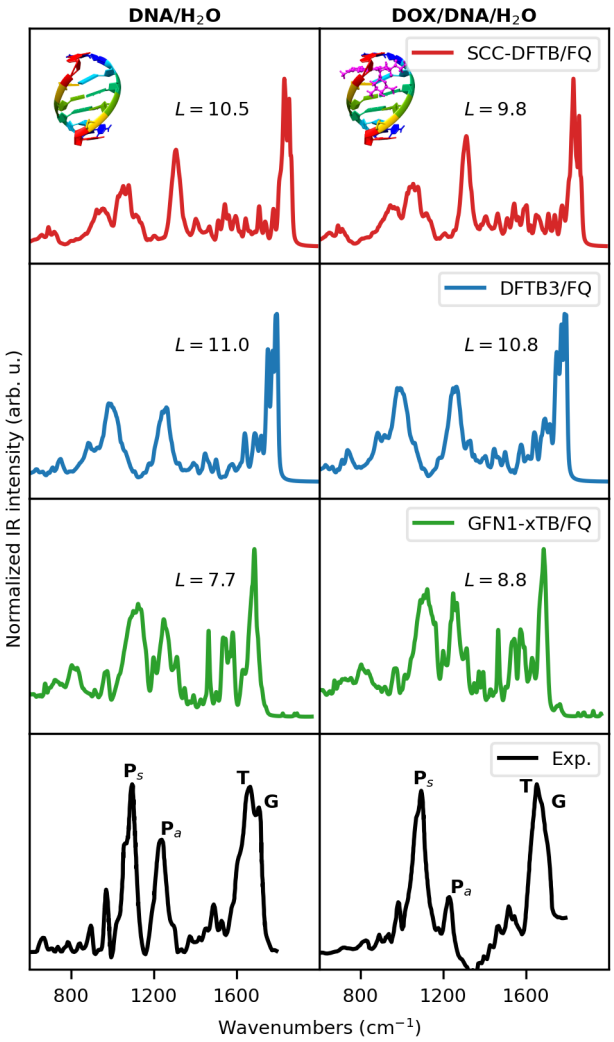

Figure S5: Convoluted IR spectra of DNA (left) and DOX/DNA (right) in aqueous solution as computed at the DFTB/FQ level with diverse choices of the DFTB Hamiltonian. Calculated spectra have been scaled by the gas-phase scaling factors reported for DFTB methods in the literature: 0.9933[1] (SCC-DFTB), 0.9993[2] (DFTB3), 0.982[3] (GFN1-xTB). Experimental data taken from Ref. 4 are reported in the lower panels (black lines). L values (Eq. 14 in the main text) are also given.

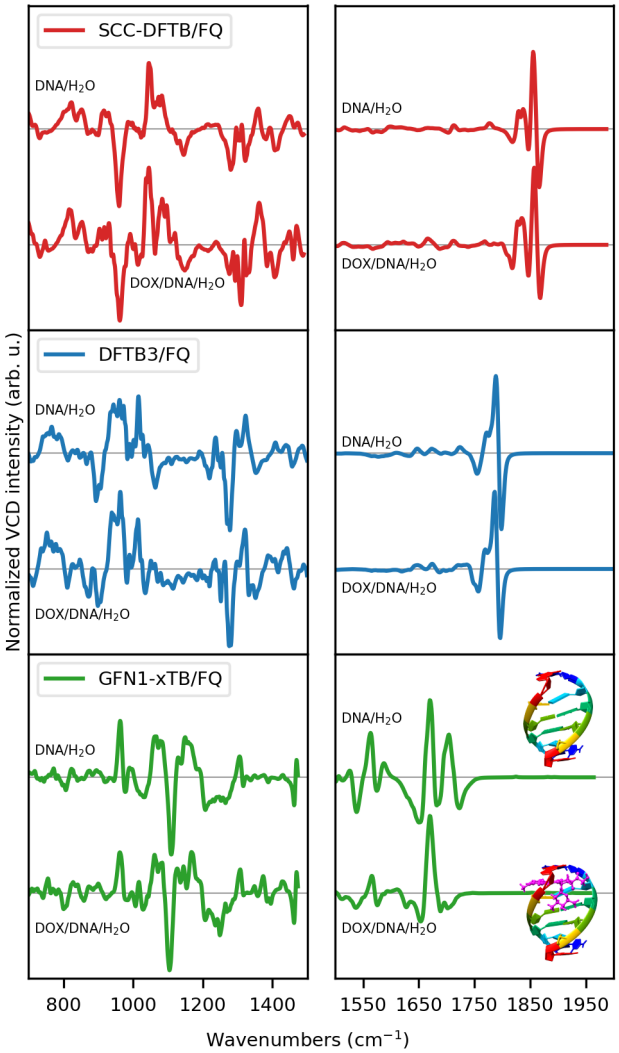

Figure S6: Medium wavenumber (1500-2000 cm^{-1}) (right) and low wavenumber (700-1450 cm^{-1}) (left) VCD spectra of free DNA and DOX/DNA intercalation complex computed with diverse choices of the DFTB/FQ Hamiltonian. Calculated spectra have been scaled by the gas-phase scaling factors reported for DFTB methods in the literature: 0.9933[1] (SCC-DFTB), 0.9993[2] (DFTB3), 0.982[3] (GFN1-xTB). Experimental data taken from Ref. 4 are reported in the lower panels (black lines).

S2 Ubiquitin in aqueous solution

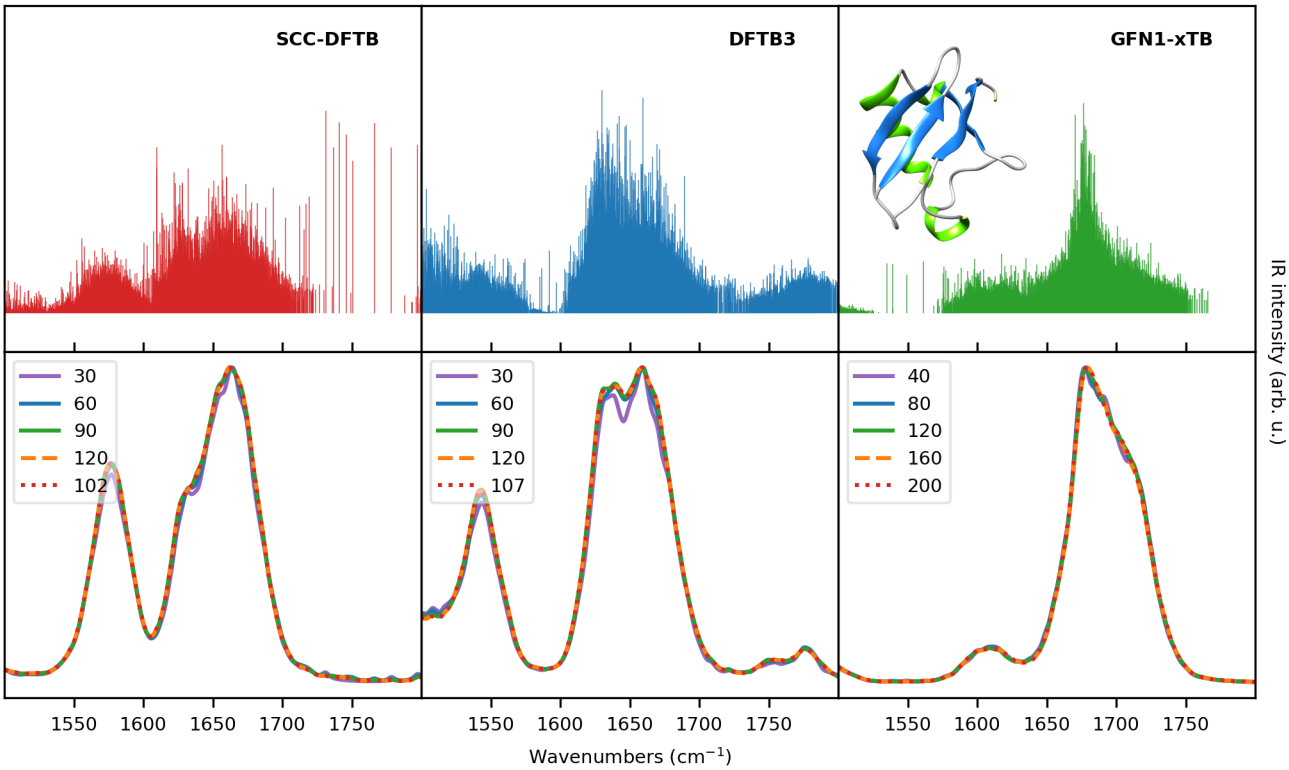

Figure S7: IR stick spectra (upper panel) and convergence analysis (lower panel) for aqueous UBI as obtained with diverse DFTB/FQ methods.

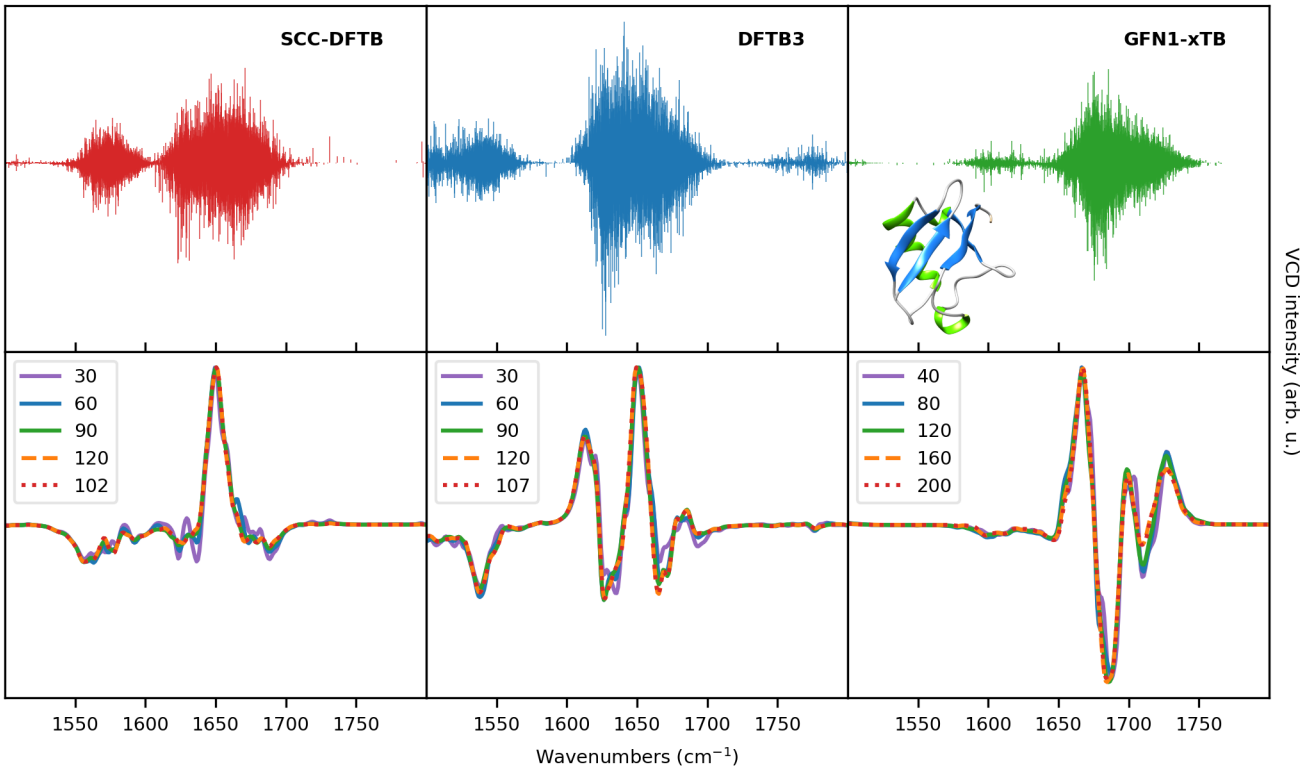

Figure S8: VCD stick spectra (upper panel) and convergence analysis (lower panel) for aqueous UBI as obtained with diverse DFTB/FQ methods.

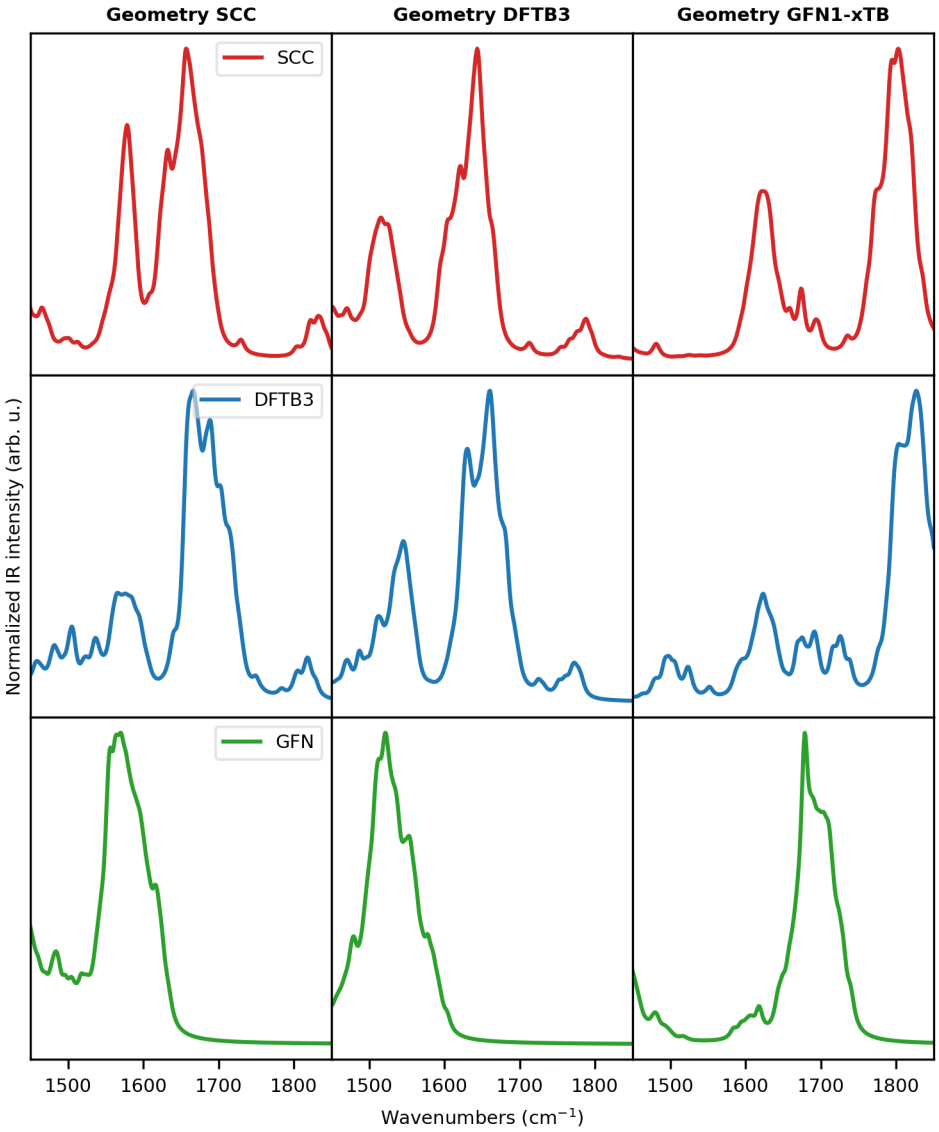

Figure S9: Convoluted IR spectra of aqueous UBI as obtained with diverse DFTB/FQ methods combined with the geometry optimized at the SCC/FQ (left column), DFTB3/FQ (middle column) and GFN1-xTB/FQ (right column) levels.

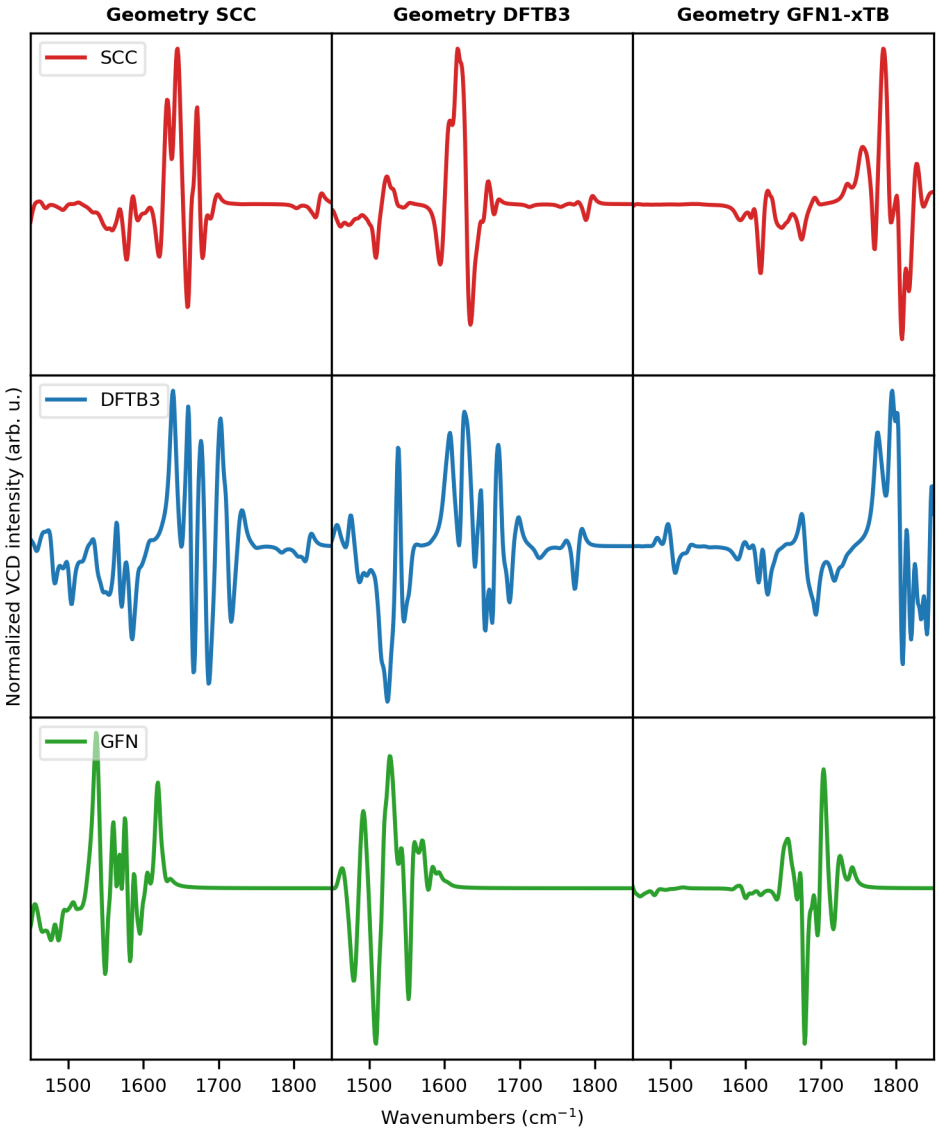

Figure S10: Convoluted VCD spectra of aqueous UBI as obtained with diverse DFTB/FQ methods combined with the geometry optimized at the SCC/FQ (left column), DFTB3/FQ (middle column) and GFN1-xTB/FQ (right column) levels.

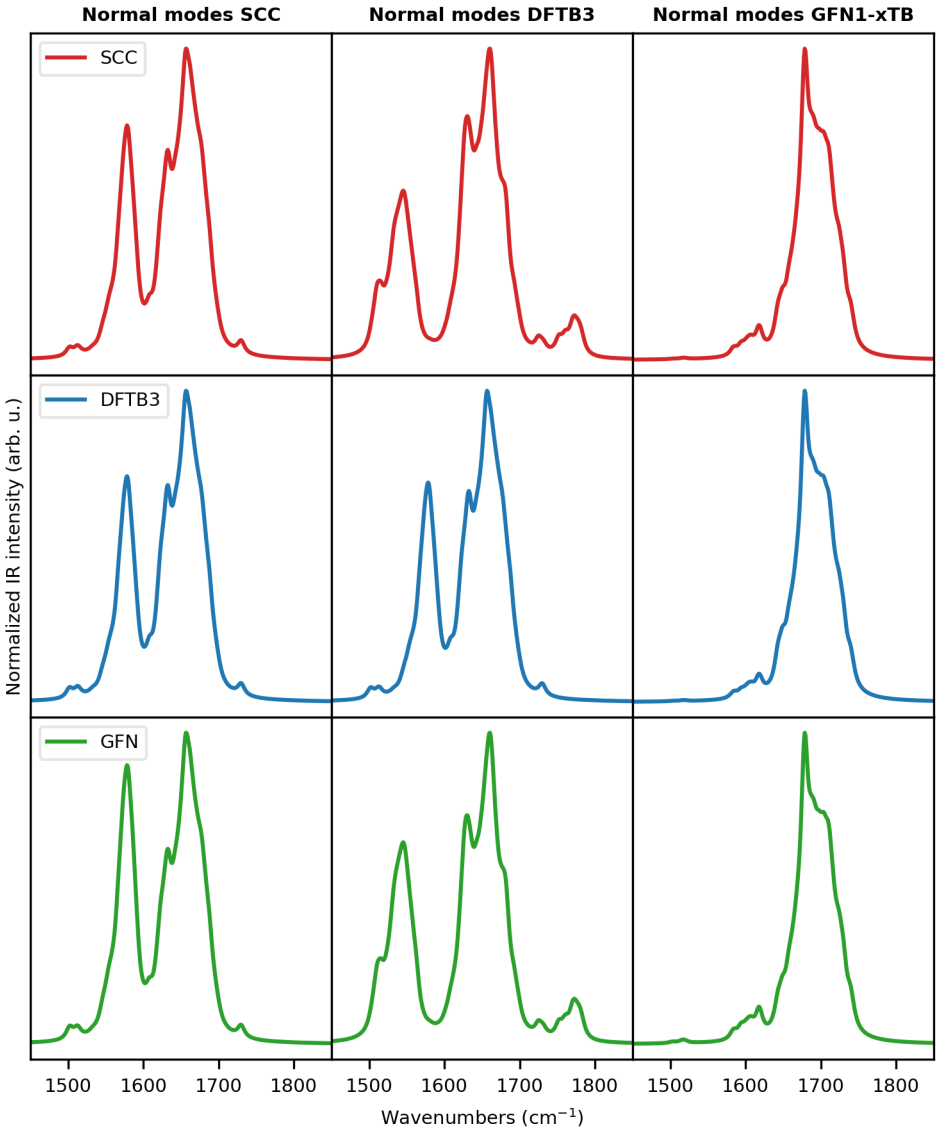

Figure S11: Convoluted IR spectra of aqueous UBI as obtained with diverse DFTB/FQ methods combined with the optimized geometry and normal modes computed at the SCC/FQ (left column), DFTB3/FQ (middle column) and GFN1-xTB/FQ (right column) levels.

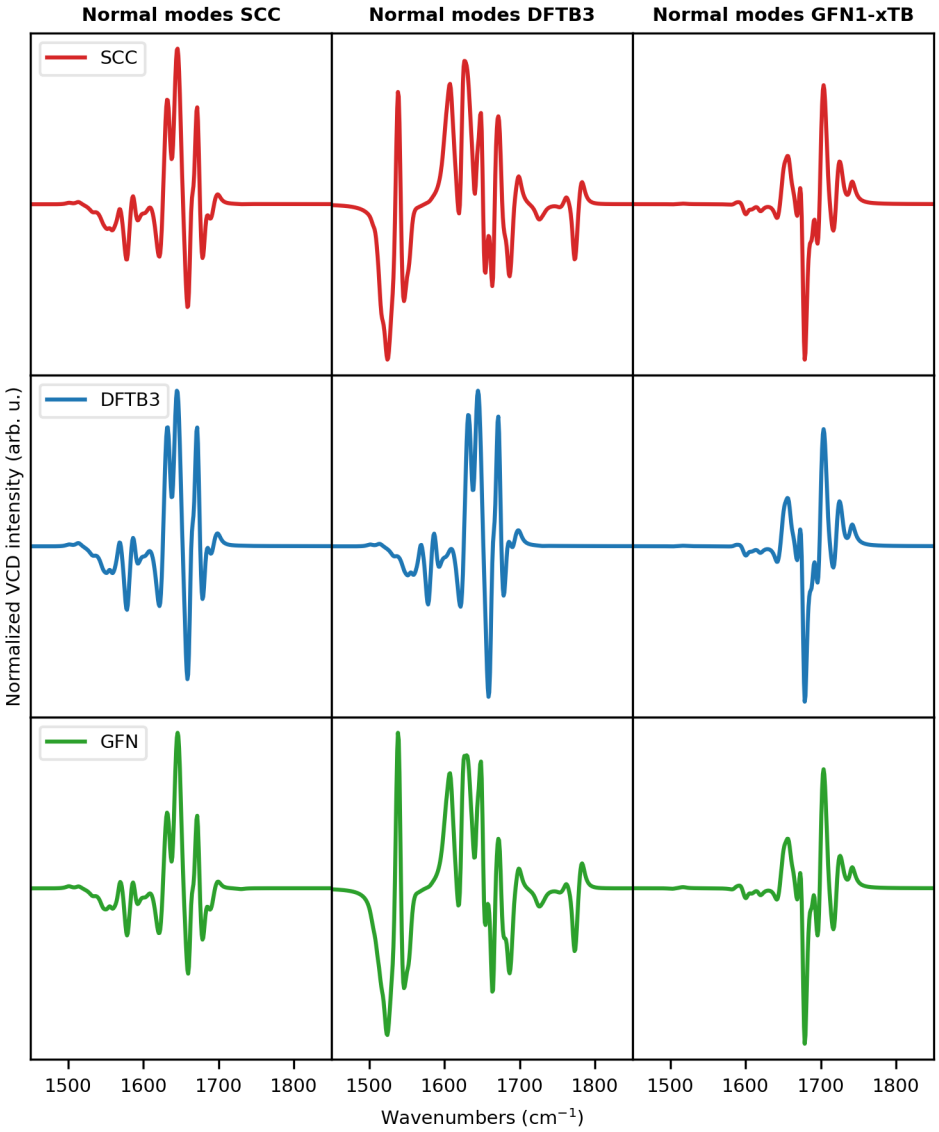

Figure S12: Convoluted VCD spectra of aqueous UBI as obtained with diverse DFTB/FQ methods combined with the optimized geometry and normal modes computed at the SCC/FQ (left column), DFTB3/FQ (middle column) and GFN1-xTB/FQ (right column) levels.

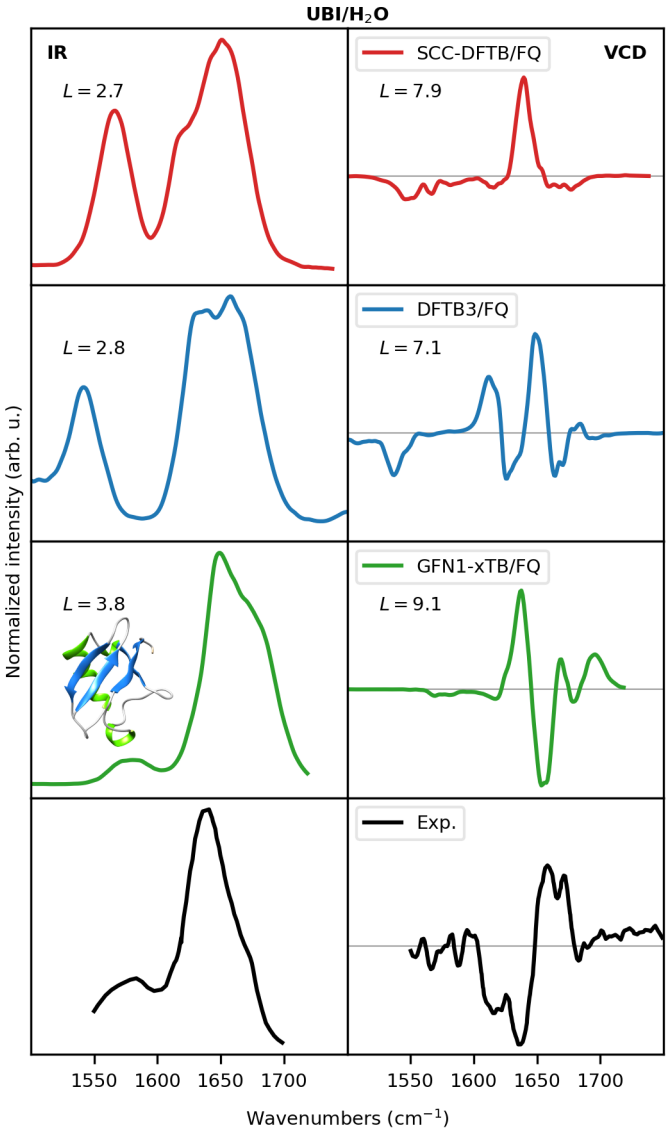

Figure S13: Convoluted IR (left) and VCD (right) spectra of UBI in aqueous solution as computed at the DFTB/FQ level with diverse choices of the DFTB Hamiltonian. Calculated spectra have been scaled by the gas-phase scaling factors reported for DFTB methods in the literature: 0.9933[1] (SCC-DFTB), 0.9993[2] (DFTB3), 0.982[3] (GFN1-xTB). Experimental data extracted from Ref. 5 are reported in the lowest panels (black lines). L values (Eq. 14 in the main text) are also given.

S3 Lysozyme in aqueous solution

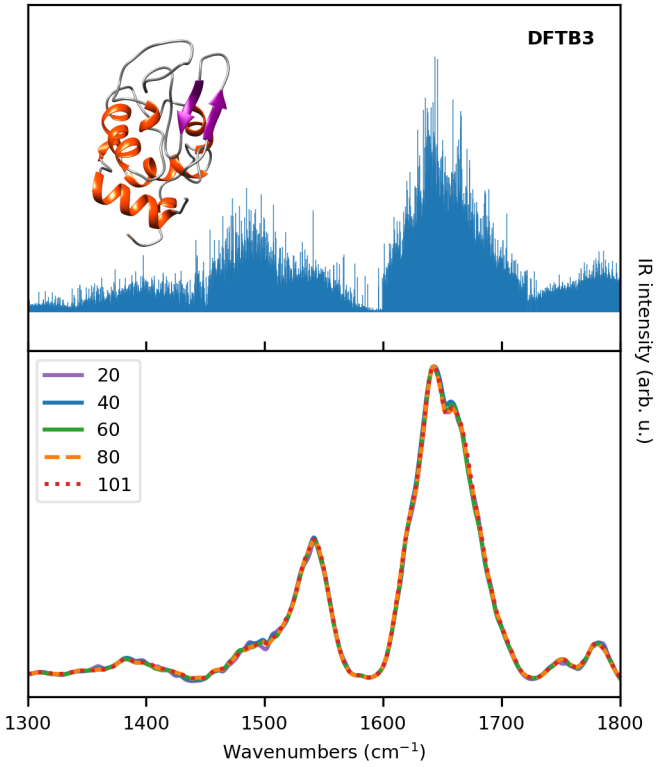

Figure S14: IR stick spectra (upper panel) and convergence analysis (lower panel) for aqueous LYS as obtained at the DFTB3/FQ level.

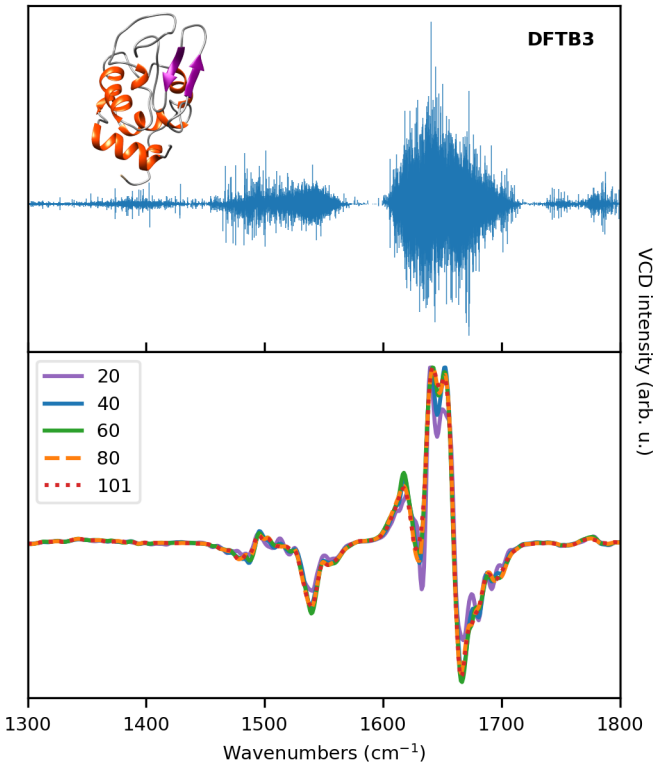

Figure S15: VCD stick spectra (upper panel) and convergence analysis (lower panel) for aqueous LYS as obtained at the DFTB3/FQ level.

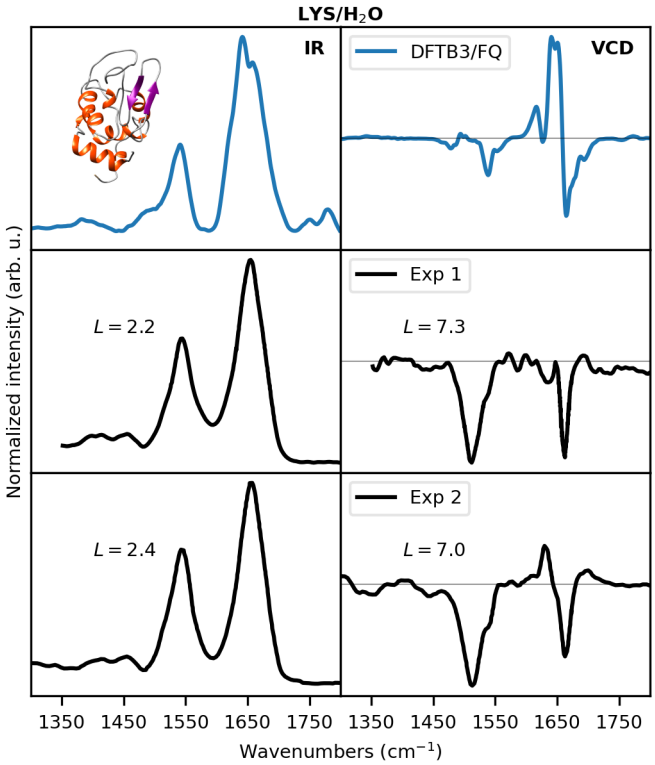

Figure S16: Convoluted IR (left) and VCD (right) spectra of LYS in aqueous solution as computed at the DFTB3/FQ level. Calculated spectra have been scaled by the gas-phase scaling factors reported for DFTB3 method (0.9993).[2] Experimental data extracted from Ref. 6 (Exp 1) and Ref. 7 (Exp 2) are shown in the lowest panels (black lines). L values (Eq. 14 in the main text) are also given.

References

(1) Witek, H. A.; Morokuma, K.; Stradomska, A. Modeling vibrational spectra using the self-consistent charge density-functional tight-binding method. I. Raman spectra. *J. Chem. Phys.* **2004**, *121*, 5171–5178.

(2) Inakollu, V. S.; Yu, H. A systematic benchmarking of computational vibrational spectroscopy with DFTB3: Normal mode analysis and fast Fourier transform dipole autocorrelation function. *J. Comput. Chem.* **2018**, *39*, 2067–2078.

(3) Pracht, P.; Grant, D. F.; Grimme, S. Comprehensive assessment of GFN tight-binding and composite density functional theory methods for calculating gas-phase infrared spectra. *J. Chem. Theory Comput.* **2020**, *16*, 7044–7060.

(4) Agudelo, D.; Bourassa, P.; Bérubé, G.; Tajmir-Riahi, H. Review on the binding of anticancer drug doxorubicin with DNA and tRNA: Structural models and antitumor activity. *J. Photochem. Photobiol. B* **2016**, *158*, 274–279.

(5) Choi, J.-H.; Lee, H.; Lee, K.-K.; Hahn, S.; Cho, M. Computational spectroscopy of ubiquitin: Comparison between theory and experiments. *J. Chem. Phys.* **2007**, *126*, 01B618.

(6) Ma, S.; Freedman, T. B.; Dukor, R. K.; Nafie, L. A. Near-infrared and mid-infrared Fourier transform vibrational circular dichroism of proteins in aqueous solution. *Appl. Spectrosc.* **2010**, *64*, 615–626.

(7) Kessler, J.; Andrushchenko, V.; Kapitán, J.; Bouř, P. Insight into vibrational circular dichroism of proteins by density functional modeling. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4926–4935.