Supporting Information

A Novel Fluoropolymer as Protein Delivery Vector with Robust Adjuvant Effect for the Cancer Immunotherapy

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The synthesis of PF

PF was synthesized according to the method in our previous report [1]. As shown in **Fig. S1**, the 2,2,3,3-tetrafluorobutane-1,4-diol (0.4 mmol) and KOH (0.3 mmol) were dissolved in 10 mL of anhydrous DMSO. After stirring at room temperature for 10 minutes, epichlorohydrin (0.8 mmol) was added dropwise to the mixture and then stirred overnight at room temperature. After the reaction, the crude product was filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (EA/PE = 1/3, v/v) to obtain the linkers referred as **F-Bridge**.

F-Bridge: 64% yield. ^{1}H-NMR (400 MHz, DMSO, TMS) δ: 2.574 (2H, epoxyresin -CH_2-), 2.74-2.76 (2H, epoxyresin -CH_2-), 3.140-3.167 (2H, epoxyresin -CH-), 3.413 (2H, -$CH_2OCH_2CF_2$-), 3.886 (1H, -$CH_2OCH_2CF_2$-), 3.915 (1H, -$CH_2OCH_2CF_2$-), 3.971-4.054 (4H,-$CH_2OCH_2CF_2$-).^{13}C-NMR (DMSO, 100 MHz) δ: 43.252, 49.932, 66.898, 67.154, 67.409,72.745, 113.662, 115.878, 116.174, 116.470, 118.687.

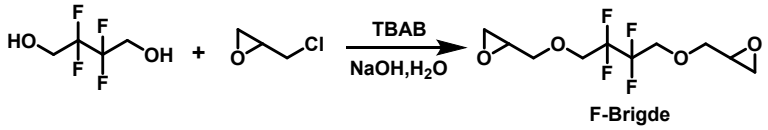

Fig. S1 The synthesis route of F-Bridge

As shown in **Fig. S2**, PEI 600 Da and **F-Bridge** (mole ratio of monomer was 1:2) were dissolved in anhydrous ethanol. The reaction mixtures were further stirred at 80 ℃ under a N_2 atmosphere for 72 h. After the reaction, the residues were dissolved in a water and dialyzed against deionized water for 3 days (MWCO 3500). The pale-yellow semi-solid products were obtained after lyophilization named **PF**.

PF：40.% yield. ^{1}H-NMR (400 MHz, D_2O, TMS) δ: 2.687-2.769 (m, 24H, -$NHCH_2CH_2N$- and -$CH_2CHOHCH_2O$-), 3.690-3.730 (m, 4H, -$CH_2CHOHCH_2O$-), 3.978 (2H, -$CH_2CHOHCH_2O$-), 4.083-4.153 (4H, -$CH_2OCH_2CF_2$-). ^{19}F-NMR (D_2O) δ: -121.650. GPC: Mw = 12.3 kDa, PDI = 1.33.

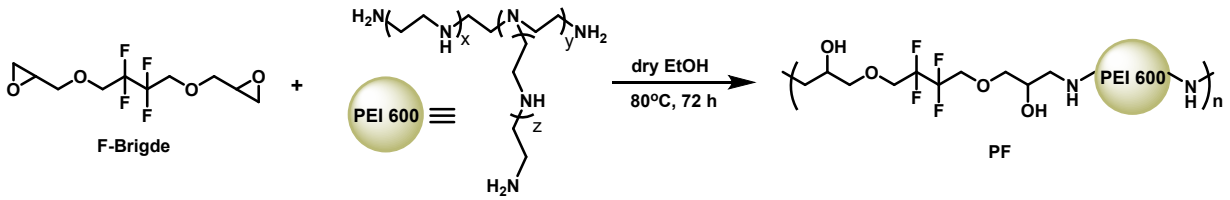

Fig. S2 The synthesis route of PF

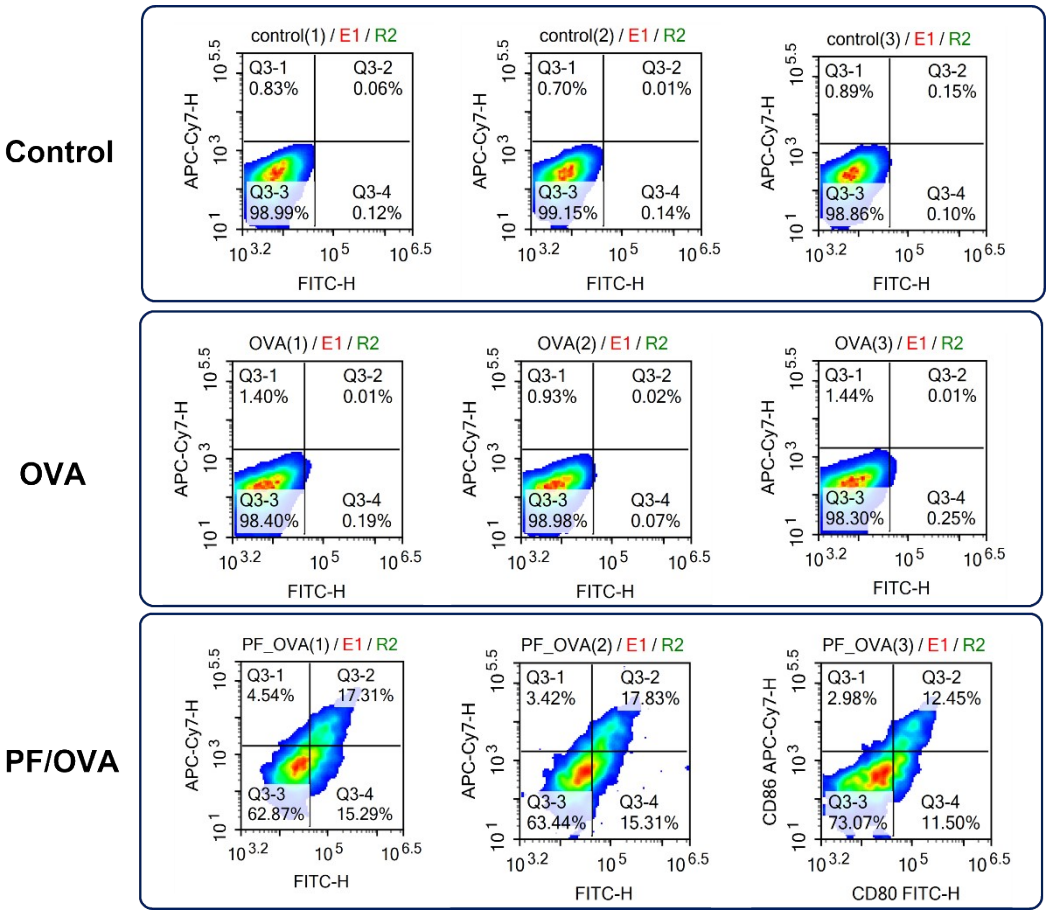

Fig. S3 The expression level of CD80/86 in the surface of DCs after different treatments for 24 h measured by flow cytometer. The data are expressed as mean ± SD (n =3).

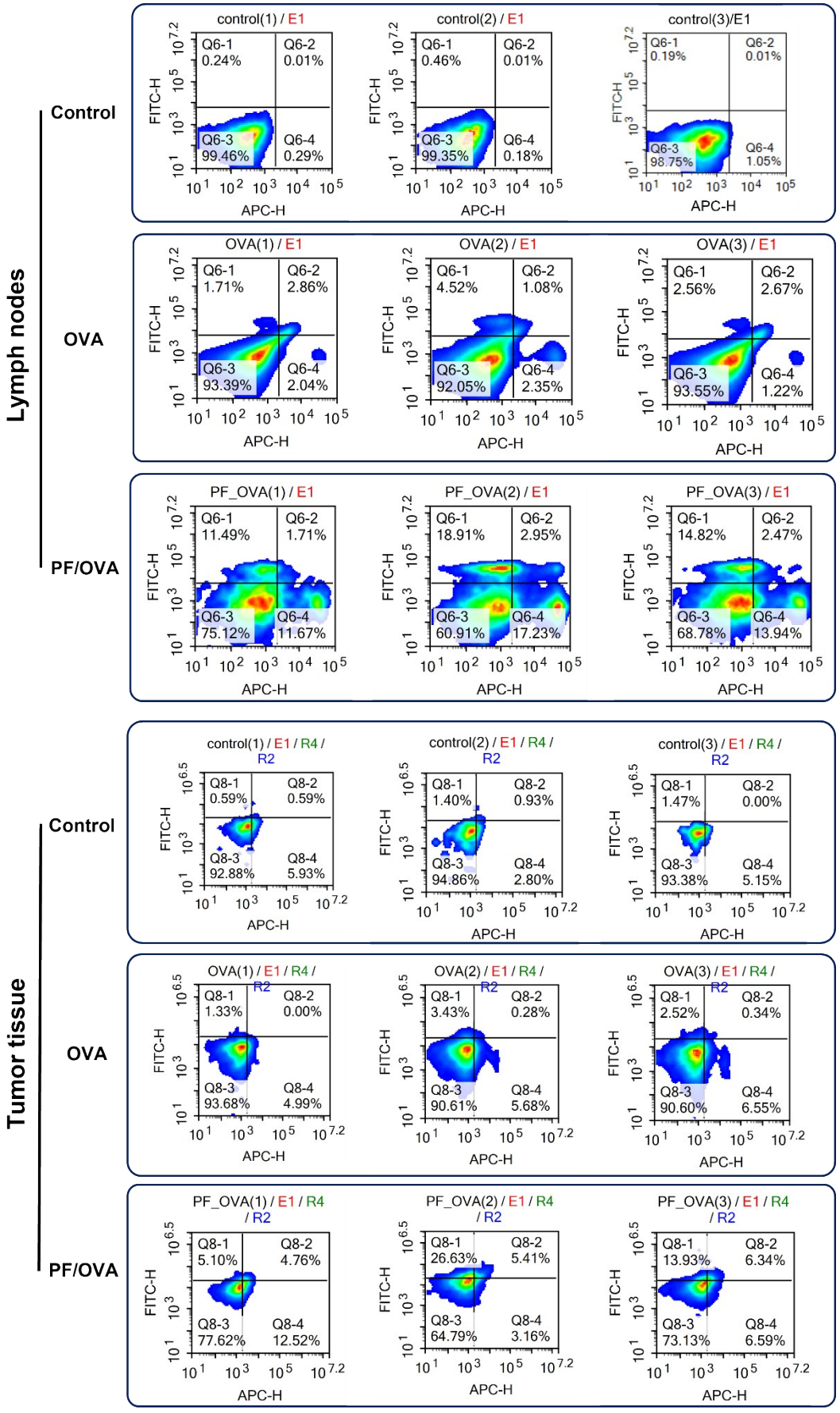

Fig. S4 The flow cytometry data of CD4+ and CD8+ T cells proportion in lymph nodes (up) and

tumors (down). The data are expressed as mean ± SD (n =3).

References

[1] Xiao, Y. P.; Zhang, J.; Liu, Y. H.; Huang, Z.; Wang, B.; Zhang, Y. M.; Yu, X. Q., Cross-linked polymers with fluorinated bridges for efficient gene delivery. J. Mater. Chem. B 5 (2017) 8542-8553.